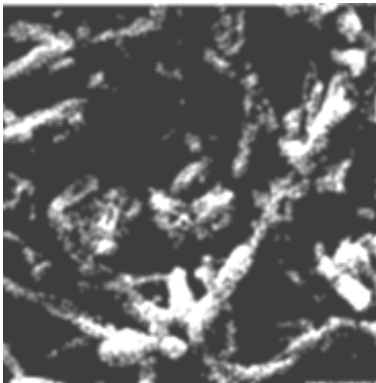
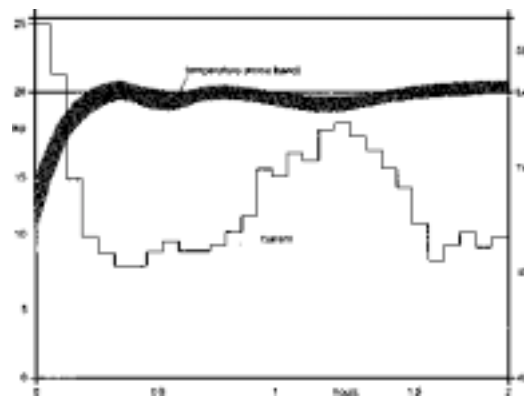

LEAD ACID BATTERY FORMATION TECHNIQUES



Dr. Reiner Kiessling



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PREFACE

When the author entered into the battery world in 1968 mercury arc rectifiers and rotary generators were still quite popular DC sources for battery charging and formation. In those days control of formation was made by timers and average current estimates and rarely could one find ampere hour meters included.

Automotive batteries in their majority were built with heavy plates in heavy hard rubber containers and the service life was accepted to be around two years. As another example, in stationary batteries open Plante type cells were still in use and received a second set of positive plates after the first set were worn out.

The world has changed dramatically since then both in design and technology. What has not changed is the role of the old lead-acid battery for rechargeable systems, to the contrary its market share has increased and there is no sign that it can be replaced near term by any other secondary battery system.

So it is worthwhile to look at improvements in the technology of battery production which have taken place primarily over the last ten years. This brochure dealing with formation is part of this progress. Thyristor technology and microprocessor control allow for methods which one could only dream about in former times.

In many discussions with battery people all around the world the author recognized that a theoretical background in many cases was welcomed. I ask that Electrochemists excuse simplifications and on the other hand production managers should realize that explanations are not always simple.

1. INTRODUCTION

The initial formation charge of a lead-acid battery, whether in the form of plates or as an already assembled battery, is quite a complex bundle of chemical reactions. It is important to know in principle about the most important parameters controlling this process in order to achieve good reproducible results with reasonable efforts.

1.1 Chemical Reactions

1.1.1 Pasting and Curing

The basic materials in battery production are lead alloys to make the grids and lead oxide for the active material. The grids are used as a support for the active material and as electric conductors for the current.

Lead Oxide - Paste

Lead oxide is produced either in Barton pots or in mills operating on a surface oxidation of lead. The oxide particles always contain some residual metallic lead which is separated and carried away by an air stream then collected in filters.

The two types of oxide generated are slightly different in their properties depending on the type of production equipment and the production parameters. These considerations are of minor interest in this context.

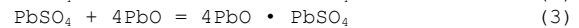
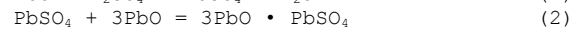
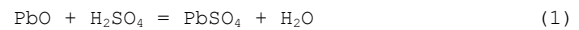
The plates for all automotive or SLI batteries and most industrial batteries are made by preparing a paste from lead oxide with fairly strong sulfuric acid then pressing this paste

into the grids. After surface drying, the plates are cured in moisture saturated air at slightly elevated temperature and then dried. The same reactions take place in tubular positive plates, but the methods of production are different.

The paste preparation and curing are very important steps and any mistakes or faults therein cannot be fully repaired later. Most problems arising in formation are due to compromises in these steps, so we must look at them.

Basic Sulfates

The initial reaction of sulfuric acid with lead oxide (equation 1) leads to normal lead sulfate and heat evolution. Under the influence of excess lead oxide and water this is not stable, so converts into basic sulfate, either tribasic (2) or tetrabasic (3) according to



Tribasic sulfate is crystallized as small needles with high specific surface and formed, roughly speaking, below 70° C. Tetrabasic sulfate forms more bulky crystals at temperatures above 70° C. Figures 1 and 2 show scanning electron microscope pictures of both types of crystals and the differences in size and shape.

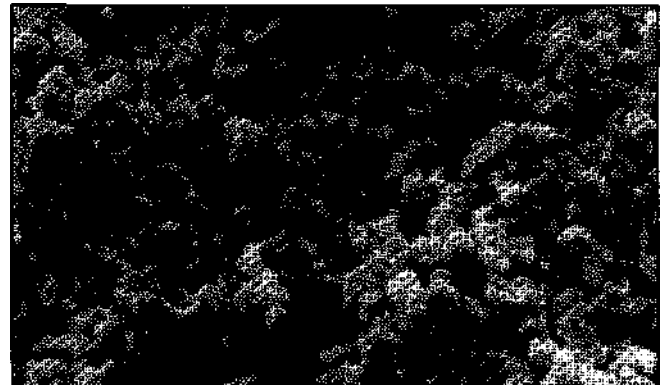


Figure 1. Tribasic Lead Sulfate
Courtesy of HAG EN Batterie AG, Soest, Germany

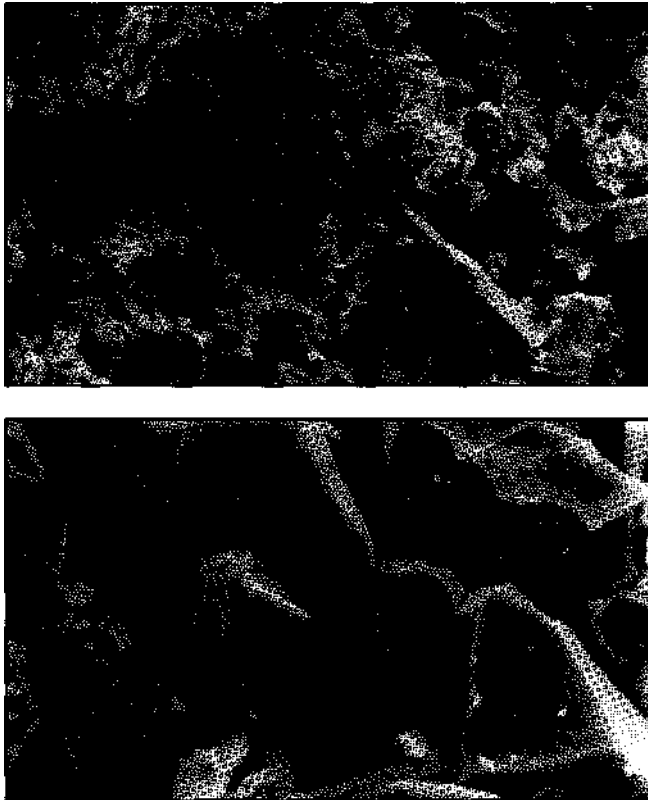


Figure 2. Tetrabasic Lead Sulfate
 Courtesy of HAGEN Batterie AG, Soest, Germany

For a problem free formation we need a high specific surface and so besides free oxide and water, tribasic lead sulfate should be the main component of the paste. This is why modern paste mixers frequently include cooling facilities as an option.

Curing

During curing no significant change is to be expected for the basic sulfates as long as the transformation temperature of 70°C is not exceeded. The important reaction happens with the residual metallic lead. This is oxidized and primarily dissolved in the paste water.

Most of it is then precipitated on the surface of the basic sulfates gluing these crystals together and mechanically stabilizing the structure. Therefore, before this reaction is finalized water loss should be avoided as much as possible.

Simultaneously, oxidation also takes place on the grid surface leading to a mechanical interlocking with the active material.

Once the oxidation of the residual lead is finalized the plates can be dried. The water will evaporate without leading to a shrinking of the active material. Without this reaction the active material would show fissures or may even fall out. The addition of fibers to the paste may exclude the worst but cover the problem rather than help to overcome it.

The active material shows a very porous structure and depending on the actual recipe, i.e. water content of the paste, the porosity is between 50 and 60% volume.

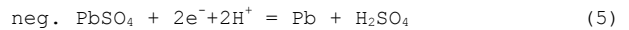
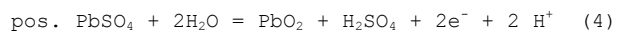
1.1.2 Formation Reactions

Under normal ambient conditions the bivalent status is most stable one for lead. Depending on the pH, i.e. the presence of sulfuric acid or sulfate, lead oxide or one of lead sulfates described above are the most favorable compounds.

Both lead dioxide and metallic lead, the final active materials in the lead-acid battery, are on a higher energy level. In order to arrive at these compounds energy must be added as occurs during a normal charge in the form of electric energy.

Formation Equations

To begin formation positive and negative plates are inserted into diluted sulfuric acid and connected to a reel. The rectifier acts like a pump removing electrons from the positive plates and pushing them into the negative ones. The following reaction equations are simplified showing only the essentials:

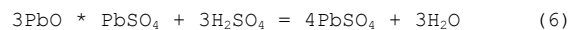


The hydrogen ions (H⁺) traveling from the positive to the negative plates close the electric circuit and leave the plates in an almost electrically neutral status.

Soaking

Before the reactions (4) and (5) can be started by switching on the current the pores should first be completely filled with electrolyte which due to capillary forces needs only minutes. Secondly one should allow for absorption of sufficient sulfuric acid to get a slightly acidic reaction (pH for better electric conductivity. This may require almost; minutes for SLI batteries and up to 2 hours for industrial batteries depending on the plate thickness.

The diluted sulfuric acid used as electrolyte will penetrate into the pores of the plates and immediately react according to equation (1) and with



the basic lead sulfates are converted into the neutral sulfPbSO₄.

This reaction is coupled with heat evolution. Per 100 g active material with the approximate composition 9 PbO PbSO₄ some 45 kJ would be evolved (also see section 2 provided the reaction could be completed immediately. 1 degree of completeness depends to a large degree on the environment and so for details we must distinguish between tank and container formation which are discussed later.

In either method the acid penetrating into the pores due to reaction is diluted to almost water. It is essential that the grid surface or, more precisely, the oxide/sulfate layer on the grid surface is wetted with electrolyte of sufficient conductivity.

The active material in this stage is a nonconductor and the electrochemical oxidation and reduction can only take place at the grid surface where the electrons can flow freely in the metal.

Lead sulfate is only slightly soluble in H₂SO₄ and only (2 mg/l) more in water. The small solubility nevertheless is essential, as the reactions can take place only in the

dissolved state. This is called a dissolution-precipitation mechanism, as the lead sulfate must first be dissolved. Then, the lead and the lead dioxide are precipitated inside the electrodes.

1.2 Formation of Negative Plates

Crystal Growth

According to the dissolution reaction



free lead ions are available directly on the interface between the metallic grid and the electrolyte. The ions pick up electrons there and are precipitated as metallic lead.

Lead does not grow in bulky crystals during electrochemical deposition but in needles with secondary and even tertiary branches. So the reaction penetrates easily into the bulk of the active material. The needle or dendrite structure is related to a large specific surface, which is necessary for a high performance battery. For formation the expanders do not play an important role. Their purpose is to maintain the large specific surface for a long period of cycling.

The acid which results from the deposition reaction (5) will react with further lead oxide or tribasic sulfate, which was covered during the soaking period with sulfate. So, until all basic components are converted, (see section 1.3) no large increase in the specific gravity of the electrolyte is to be expected inside the negative plates and therefore additional heat is generated.

Figure 3 shows more details, but is limited to automotive battery plates and is not valid for industrial plates. So the sulfate content rises up to some 25% of the theoretical formation charge and after 70% only the oxide content becomes negligible.

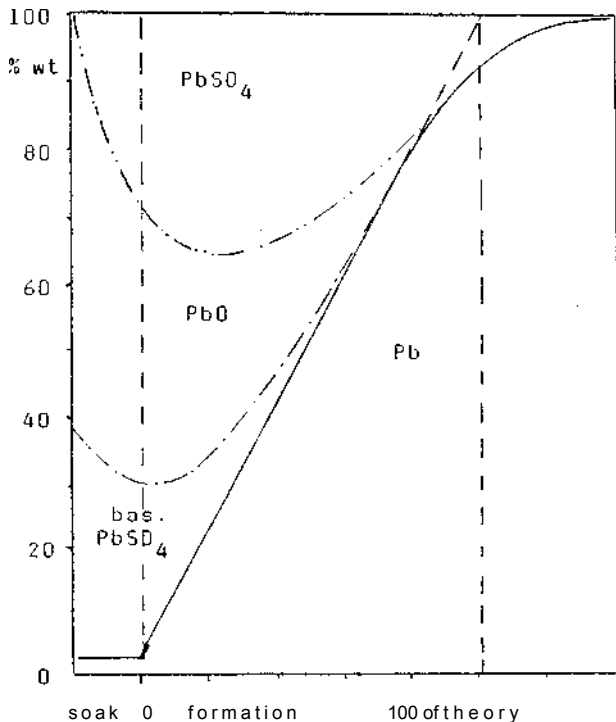


Figure 3. Composition Changes in Negative Plates during Formation

Pore Volume

One of the striking effects in formation is the change in porosity. While lead oxide has a specific gravity of 9.5 g/ml, the resulting lead has 11.3 g/ml. The weight is reduced from 223 g to 207 g per Mole and the volume of the solids is reduced to a residual volume V_r of

$$V_r = \frac{100 - 9.5/11.3 - 207/223}{11.3} = 78\% \quad (8)$$

As with the basic sulfates, the specific gravity relations are similar and the weight losses even higher, roughly speaking the volume of the solid is reduced to 75% of its original value and the porosity p increased accordingly to

$$P_{\text{formed}} = 0.25 + 0.75 \cdot P_{\text{unformed}} \quad (9)$$

The variation of porosity is also shown in figure 4. During soaking it is the formation of low density neutral sulfate that reduces porosity and hampers further penetration of acid into the bulk material. Due to "growth" of the plates and total reduction of solid volume the porosity at the end of formation is normally even higher than calculated by (9). This growth also depends on what the design will allow.

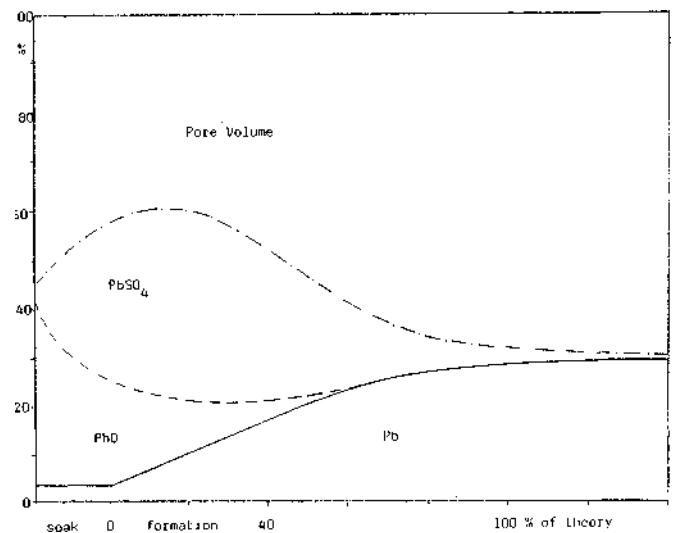


Figure 4. Porosity Changes in Negative Plates during Formation

Theoretical Charge

It is quite normal to calculate the amount of formation charge in Ah/kg of dry cured mass. For this one must know the exact recipe. In order to show the method a typical example (table 1) will be used.

Table 1. Typical Negative Mass Composition Based on 100 kg lead oxide (metal content 25%) the additives are

14.0 kg water
2.5 kg sulfuric acid
0.6 kg barium sulfate
0.6 kg expanders
0.2 kg lamp black

The 100 kg lead oxide are equivalent to 94.6 kg of lead. The reaction of the sulfuric acid with lead oxide leads to theoretically 24.8 kg tribasic sulfate and after curing 79.2 kg lead oxide (neglecting the residual metallic lead) plus the expanders (1.4 kg). The average residual moisture after the drying is assumed to be 2.5% So the active material weight AM in this stage is

$$AM = (24.8 + 79.2 + 1.4) / 0.975 \quad (10)$$

$$= 108.1 \text{ kg}$$

With 26.8 Ah equivalent to 1 electron-mole and so with 2 x 26.8 Ah equivalent to 1 Mole of lead (207 g) the 94.6 kg of lead represent a theoretical formation requirement f_{th} of

$$f_{th} = (2) (26.8) (94,600/207) \quad (11)$$

$$= 24,500 \text{ Ah}$$

Using the dry active mass as a base this results in the weight specific theoretical charge requirement F_{th}

$$F_{th} = 24,500/108.1 \quad (12)$$

$$= 226.6 \text{ Ah/kg}$$

Efficiency

The formation efficiency for the negative plates is quite high. The current conversion is very close to 100% up to some 200 to 210 Ah/kg depending on the actual current density. Only after this the side reaction of hydrogen evolution



starts to gain some influence. This reaction is kinetically hampered on a lead surface and therefore is connected with an overvoltage. The overvoltage can be seen in figure 5 as an increase in cell voltage or, if an auxiliary electrode like cadmium is used, by a more negative potential on the plates.

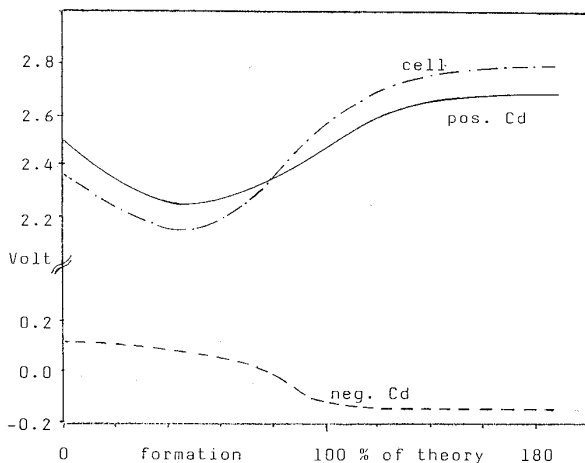


Figure 5. Cell Voltage Behavior during Formation including Half Cell Potentials against Cadmium

In general the formation of negative plates is not the problem. Practically all formations in practice are controlled by the positive plates, except when production runs out of balance and additional negative plates are to be formed.

Figure 3 includes an example of the efficiency achieved with negative SLI plates. After charging 100% of the theoretical value approximately 95% of the active material converted. This is sufficient in most cases and as the diagram also shows, the remainder can only be transferred at a low efficiency.

1.3 Formation of Positive Plates

1.3.1 Theoretical Aspects

As we have seen with the negative plates and also will positive active material formation is possible only via dissolved lead ions according to equation (6). Again, free acid is formed (4), which reacts further with tribasic sulfate and lead oxide to regenerate the lead sulfate consumed which leads to more heat generation.

But here lead dioxide PbO_2 is formed. Oxides normally are insulating materials, with some exceptions, and lead dioxide is one of those. To understand this it is necessary to look into the structure of the crystals.

Lead Dioxide a Semiconductor

The oxygen ions are negatively charged with two excess electrons compared with the neutral atom. These electrons cannot be attracted by the positive charge of the nucleus; the same amount as in the neutral atom and so the oxygen ion is quite a big one.

On the other hand, PbO_2 has a four electron deficit. The residual electrons are even more attracted by the nuclei than in the neutral atom. So the tetravalent lead is a fairly small ion despite its high atomic weight.

Therefore one tetravalent lead ion is to be replaced (formed) by two bivalent ones in order to maintain electrical neutrality their additional two electrons can travel through the crystal lattice easily leading to electrical conductivity.

This is a typical property of lead dioxide. It is a "nonstoichiometric" oxide and a semiconductor. In chemical analysis of battery lead dioxide one will find a dioxide content of 96% maximum. This means an excess of 2% lead or, in chemical formula terms,

Alpha and Beta PbO_2

Two modifications of lead dioxide differing slightly in the arrangement of the ions in the crystal lattice are known and also found in batteries. These are alpha and beta PbO_2 .

The alpha modification is found as a somewhat compact crystal agglomerate. It is the only one formed in alkaline conditions and preferably in low concentration sulfuric acid at elevated temperature. Discharge is possible only with low current density due to its compact configuration and low specific surface.

The beta modification shows small crystals, which hardly stick together. It is formed preferably in acidic conditions at low temperatures. Due to its large specific surface it can be discharged with high current density. The tendency for active mass shedding is much higher than that of alpha PbO_2 .

Fortunately or not, in spite of the initial formation structure during service life an equilibrium is reached consisting of some 20% alpha and 80% beta lead dioxide. The beta gives

the performance and the alpha acts as a glue. A couple of cycles is necessary to come to the equilibrium, the number depending on the plate thickness. So the alpha/beta problem is more important for the initial properties of lead-acid batteries. Nevertheless for automotive and stationary batteries this means a lot.

Crystal Growth

Crystal growth is another very important consideration for formation. Lead dioxide in its structure is similar to the normal oxide and so its crystals tend to grow on the oxide surface. Once this surface is covered, it is difficult for the reaction to continue.

With the small tribasic needles this is not that serious, but the much larger tetrabasic ones are covered quite early and make the formation difficult to complete.

Figures 6 and 7 show scanning electron microscope pictures of formed positive mass. The visible surface is beta-PbO₂ only. The crystal shape reproduction of the tetrabasic sulfate by surface covering of the original ones by PbO₂ can be seen clearly by comparison with figures 1 & 2.

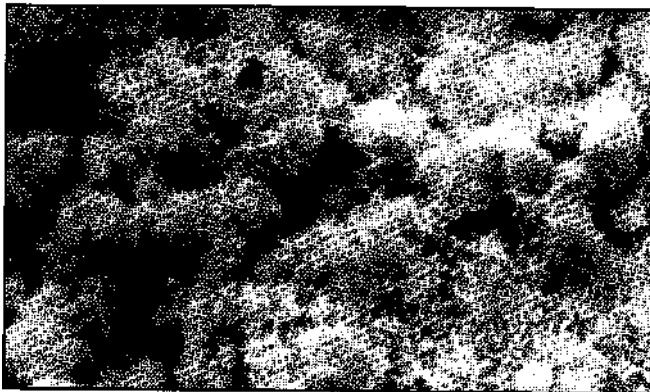
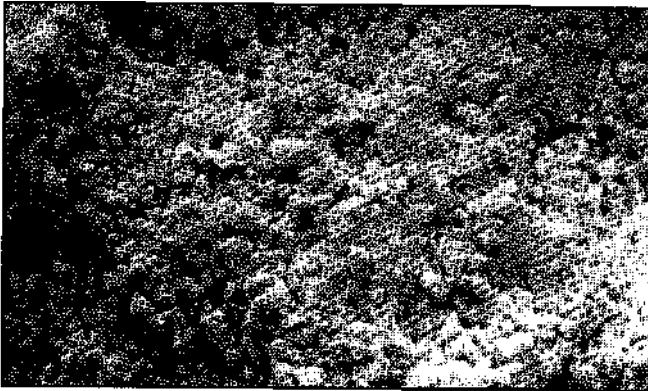


Figure 6. Positive Mass Formed from Tribasic Lead Sulfate
Courtesy of HAGEN Batterie AG, Soest, Germany

As a consequence, in the production of positive plates, i.e. paste preparation, curing and drying, temperatures above 60°C should be avoided. Paste preparation requires special attention in this respect as corrections later on are almost impossible.

After Formation



After Formation and a Discharge/Charge Cycle



Figure 7. Positive Mass Formed from Tetra and Tribasic Lead Sulfate
Courtesy of HAGEN Batterie AG, Soest, Germany

1.3.2 Practical Aspects

Soaking

During the initial soaking period the liquid reaching the center of the plate will not contain sulfuric acid anymore as this has already reacted with the free lead oxide at the surface. The chemical status is slightly alkaline (approximately pH 9) and the solubility of the lead is fairly high since no sulfate ions are present.

If the formation current would be switched on now, only alpha PbO₂ would be generated. Some rest period must be allowed during which sulfuric acid can penetrate into the plates by diffusion. This process is accelerated by elevated temperature and so the reaction heat resulting from the neutralization of the acid shows some benefits. The soaking period should be adapted to plate thickness and so treatment of industrial plates will therefore differ from automotive ones. Automotive plates typically require a soaking period of 30 minutes.

Even with long soaking time and excess sulfuric acid available the conversion of the lead oxide and the tribasic sulfate into neutral lead sulfate will remain incomplete. This results from the change in porosity.

Porosity

The specific gravity of lead oxide is 9.5 and that of sulfate 6.9 g/ml. This is combined with a weight increase from 223 to 303 g/mole resulting in a volume increase by the factor f_{vol} of

$$f_{vol} = (9.5/6.9) (303/223) = 1.87 \quad (14)$$

which would completely block the existing pore volume. On the other hand this represents the stable chemical situation. Overdoing the soaking may result in severe preformational shedding due to mechanical stress on the structure by the volume increase. The positive plates are more sensitive to this problem than the negative plates.

Figure 8 shows the porosity changes in a positive automotive plate. It is less dramatic compared with the negative ones. First of all, according to the recipe given above it is more voluminous from the beginning and the sulfate content is already higher.

As the specific gravities of lead oxide (9.5 g/ml) and lead dioxide (9.4 g/ml) are almost identical and the weight increase

(223 g/Mole to 236 g/Mole) is compensated for the loss of SO_3 , the porosity balance at the end of formation will return to the starting point.

Alpha and Beta PbO_2

When the current is switched on, throughout the plate electrolyte is close to neutral and so the initial lead dioxide formed is of the alpha type. Once the acid liberated is no longer absorbed by the PbO (and $3PbO \cdot PbSO_4$), an increasing percentage of beta is generated. This starts 10% of the theoretical transformation provided that a pre-soaking period was allowed for and the formation current high enough.

The final relations between alpha and beta PbO_2 depend highly on the average acid concentration throughout the formation. So this point will be picked up again, when looking at specific processes.

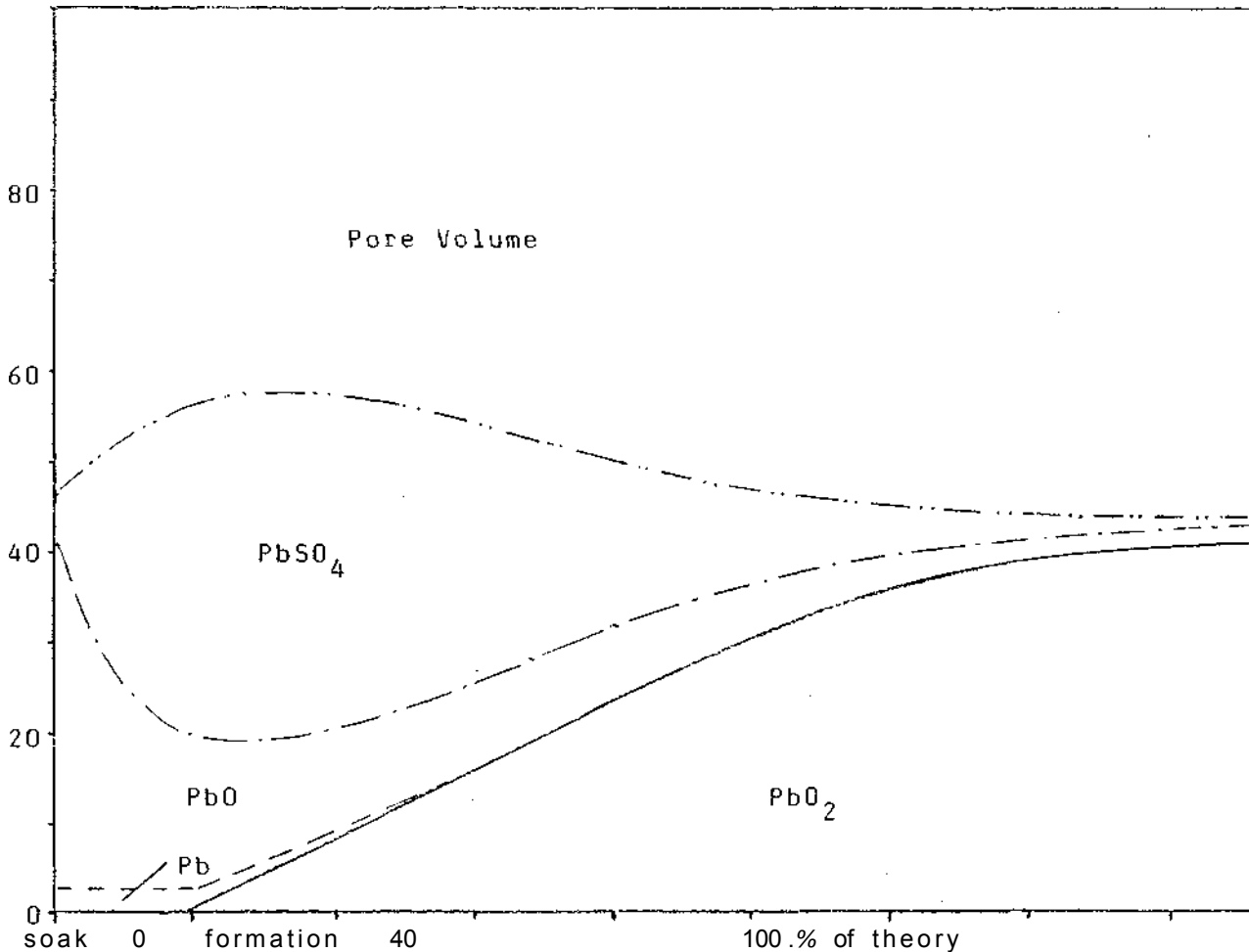


Figure 8. Porosity Changes in Positive Plates during Formation

Theoretical Charge

The theoretical formation charge can again be calculated from the mass formulation. A typical positive paste composition is given in table 2.

After curing and drying the composition is approximately equivalent to 9 PbO per PbSO₄ due to oxidation of the residual lead. This composition is used later for calculations on heat evolution during soaking.

In a different way the composition might be expressed as shown in table 2.

Table 2. Typical Composition of Positive Paste

Based on 100 kg lead oxide (25% residual metallic lead) Approximately

4.5 kg sulfuric acid (= 3.67 kg SO₃)

16.0 kg water

0.2 kg fibers are

added.

With 101.9 kg PbO plus the SO₃ from the sulfuric acid and a residual moisture after drying of 2.5% the resulting total weight of AM active material is

$$AM = (101.9 + 3.67) 70.975 \quad (15)$$

$$= 108.3 \text{ kg}$$

The 108.3 kg includes 94.6 kg lead and so the theoretically required charge f_{th} is

$$f_{th} = (2) (26.8) (94,600/207) \quad (16)$$

$$= 24,500 \text{ Ah}$$

as with the negative plates and in a similar way the charge per kg F_{th} is

$$F_{th} = 24,500/108.3 \quad (17)$$

$$= 226.2 \text{ Ah/kg}$$

Efficiency

In contrast to the negative plates the positives start to show a significant side reaction after 50 to 60% of the theoretical charge, which is oxygen evolution according to



Furthermore most battery makers use some excess of positive paste (molar Pb ratio pos/neg >1). So the positives are the plates determining the required charge amount.

Even after charging in excess of 200% of the theoretical ampere hours the active material will incorporate residual lead sulfate and as discussed above, an oxygen deficit (or excess lead) in the PbO₂. This is also called "residual PbO" in analysis reports.

Figure 9 shows the changes in composition of the active material during formation for automotive plates following the recipe given above. With some variance around 85% lead dioxide content can be achieved within 120% of the theoretical charge. Unfortunately this value also depends on the oxide quality and the plate thickness.

So it is a matter of compromise between top performance and steeply rising formation costs, where and when to stop positive plate formation. More detailed discussion will be given in the following chapters.

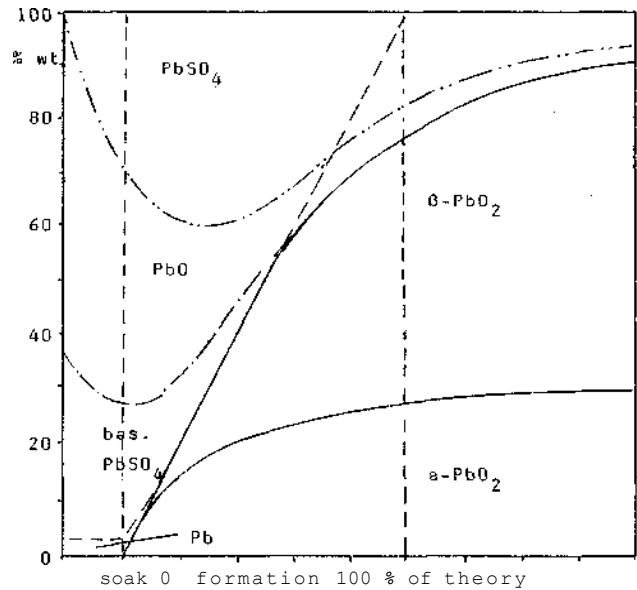


Figure 9. Composition Changes in Positive Plates during Formation

2. Plate Formation

2.1 Formation Set-up

Formation Tanks

To do formation of plates in batches after curing and drying is called tank formation. It is the traditional method and still is popular for industrial plates. The old ceramic containers have been replaced by hard rubber and PVC plastics.

For automotive battery production hard rubber containers (or tanks) are commercially available items, while for industrial plates cell jars can be used. Frequently, tanks are made according to battery manufacturers design, and therefore many different designs are in use.

In order to bring them up to suitable operating level (ergonomics) and to provide sufficient electrical insulation they are set up on insulator blocks, made of porcelain or other acid resistant material.

Installation

Normally a U-Shape arrangement for the cells in series is used, which reduces cable length to the rectifiers. Many people on the other hand believe this layout should be avoided for safety reasons since a voltage in excess of 120 V DC exists between end tanks placing the operator in serious danger. Additionally there might be dangerous leakage currents between the final tanks. So the safest method is to set-up tanks in one row with one short and one long cable.

In recent years hoods above the tanks connected to exhaust fans have become a standard. They are either made of plastic foils to be rolled up during handling or of rigid PVC which can be tilted for access. The exhaust fans are not only to vent the acid fumes resulting from gassing

but also to keep the hydrogen concentration (equation 12) below 2% in the forming area. Otherwise explosions or fire may occur.

Despite the dramatic improvements of environmental conditions in the formation room, it is still necessary to provide an acid resistant floor, as some spillage will occur. The need for regular washing with water is obvious.

The plates are inserted by alternating positives and negatives into grooves provided on the long side walls of the tanks. SLI plates are formed as unbroken panels, usually two or three in one groove. Industrial plates are formed one by one and the tanks are not always provided with grooves.

2.2 Traditional Contacting

The traditional method for plate connections is to tack weld (tack) them to lead bars or forming wire on top of the tanks and to make the intercell connections with additional short lead bars. This method ensures that a good connection is made for the entire formation period.

Nevertheless some plates or panels may not be tack welded well enough requiring retacking of those plates. This can be done, if it is recognized that plates are not changing color. However retacking should not be attempted when other plates are already gassing, releasing explosive hydrogen.

Parallel formation rows should be set to the same potential by interconnecting the negative ends.

2.3 Tackless Formation

The tacking of the plates to the paralleling bars and the intertank connections are labor intensive processes which can now be avoided for automotive production. Usually industrial plates are formed in the traditional way. Special equipment required for tackless formation is commercially available for automotive plates.

Special Tanks

The specific tanks used by the SIC company in Switzerland are shown in figures 10 and 11. Basically the tanks are made of hard rubber. The current feeding lead bars are mounted on one side of the tank from the top down close to the bottom and horizontally across leaving some sediment space on the bottom. Inserts, made of hard rubber, provide the grooves where the panels are often inserted in doubles but sometimes triples. They are adjustable to the width of the panels.

As shown in figure 11 the bars are machined to a 30° slope at the contact area with the lugs of the panels and further precautions are made to ensure good electrical connection.

Activation of Contact Bars

Once the formation tanks are set up the bars need surface preparation by cycling at least 5 times with 5 Amps for 2' i.e. feed through the tanks 5 Amps in one starting direction for 24 h, then reverse the current for another 24 h and so on. This gives a surface oxidation and reduction providing soft and spongy layer for the lugs. After the last cycle the bars are positive (PbO₂ covered) and negative (Pb sponge covered). With 5 amperes flowing the panels are then inserted into the grooves, the negative plates with the lug facing positive bars and lugs of the positive plates rest on the negative bars. During insertion allow the panels to fall onto the bars for the last 10 to 15 cm. Continue to charge the bars with 5 amps.

Reverse Charge

Once all of the plates have been inserted, the reverse formation is continued for about an hour with a current of 100 amps. This process oxidizes the negatives and forms metallic lead at the contact point of the positives insuring good positive contact.

Then the current is reversed or in older installations the plates discharged to zero voltage, and formation is started the normal way.

The bars change polarity with each formation run and so the plates must be inserted in alternating directions. Normally this is indicated by the rectifiers according to their red and green status lights.

It should be noted that due to the polarity change high voltage differences between two rows (circuits) might occur at opposite sides of the forming row.

2.4 Rectifiers

Rectifiers allowing for more or less constant current only by control through a saturated core for an adjustable time are phasing out. Besides their inflexibility they have a low energy efficiency (ca. 80%) and with this the energy cost high and additional cooling is required.

They were replaced in the 60's with multiple thyristor stacks each delivering a defined constant current and separately switchable by program cards. With a proper set of different nominal currents it became possible to realize multistep constant current/time formation programs.

This technology has greatly improved with precise phase control of thyristors and computerized control of formation schedules. Introduction of programmable microprocessors with data storage led to the DIGATRON BAFOS and FCI Micro-Form systems, which allow use of any reasonable parameter for formation control.

Tackless formation is now made with converter/inverter systems instead of simple rectifiers and the energy stored during reversal is regenerated to the power source.

Further details will be discussed with the applications.

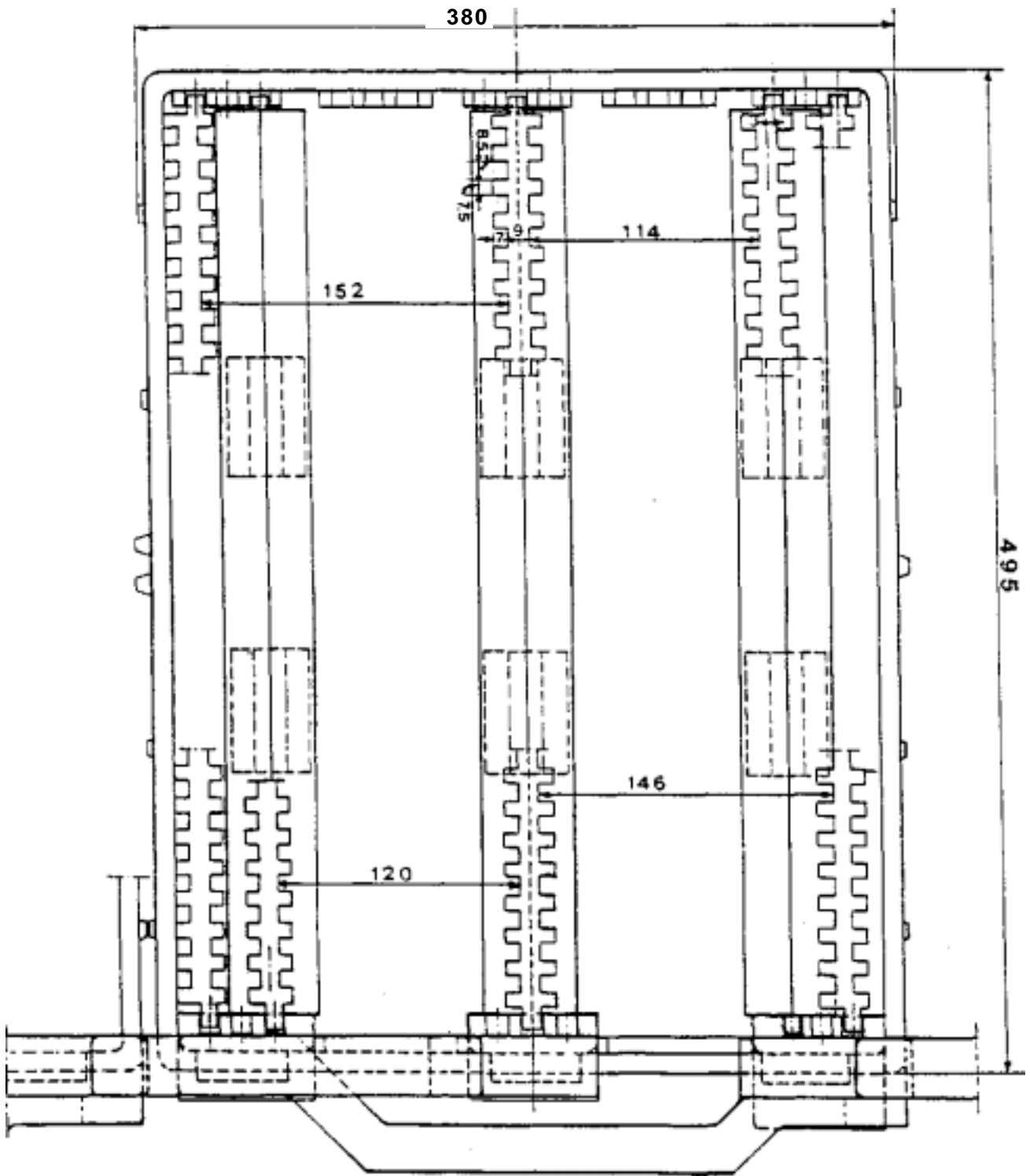


Figure 10. Forming Tank, Top View

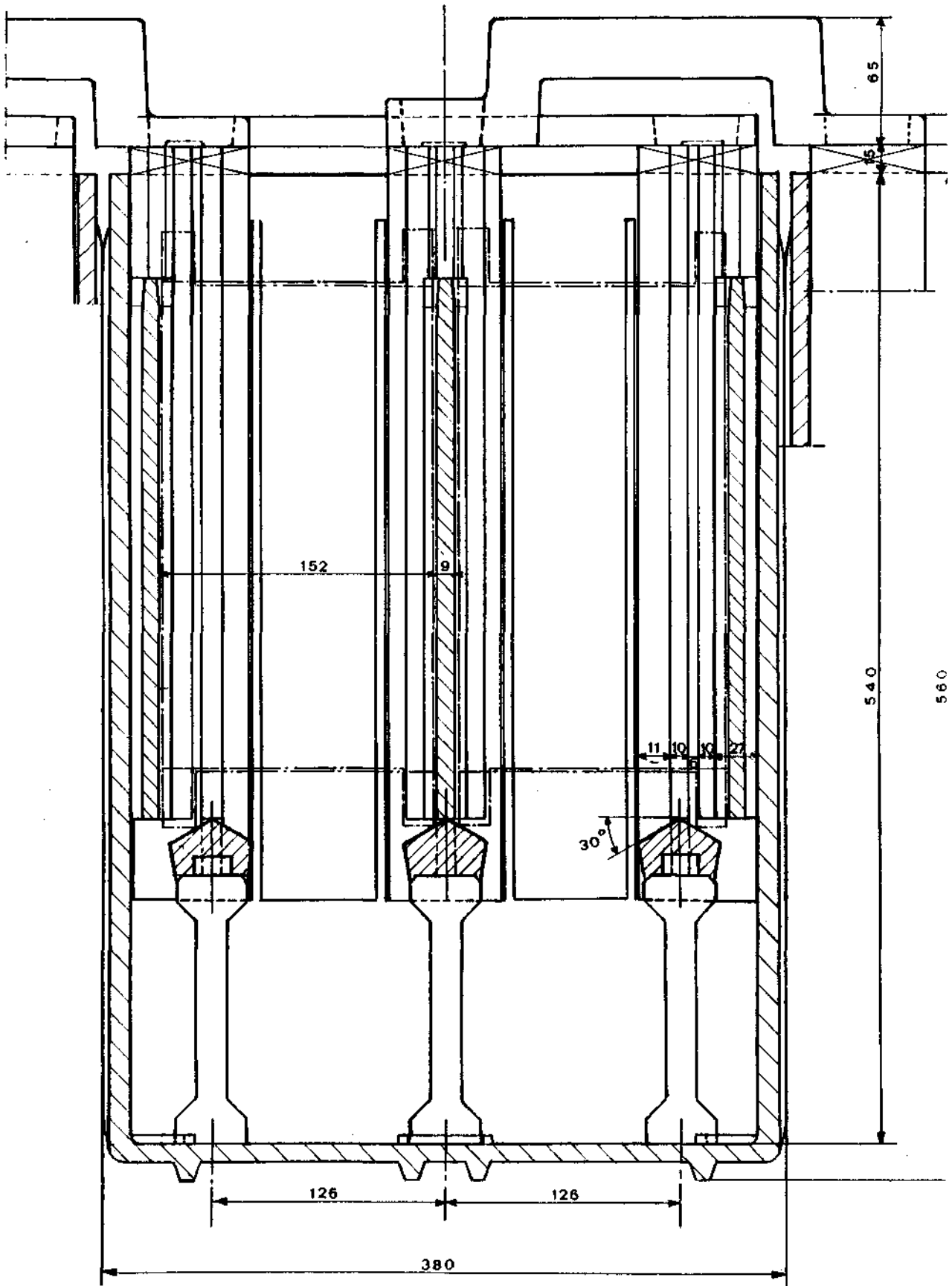


Figure 11. Forming Tank, Side View 10

2.5 Temperature Aspects

2.5.1 Heat Sources

Neutralization

The chemical basics were explained in chapter 1.1.2. The first heat source is the transformation of lead oxide and of the basic lead sulfates into neutral lead sulfate giving 45 kJ per 100 g of active material based on the composition in tables 2 and 3.

For an example of tank formation, the heat capacity of lead and lead compounds is negligible compared to the electrolyte and so the temperature increase depends on the relation of active material to the amount of electrolyte.

Table 3. Heat capacity of active components for the neutralization reaction

Compound	Amount [g]	Heat cap. [J/°C]
grid	45	6
lead oxide	81	13
lead sulfate	19	17
sulfur acid	45	-
water	375	1,585
		total 1,621

The above relationship varies to a large extent, so only an example can be given using the same material composition of 9 PbO per PbSO₄ from table 2 and a 1.08 g/ml (= 12% wt) sulfuric acid as starting condition for the electrolyte. This leads to the data of table 3.

First of all it is confirmed that besides the water content in the electrolyte the contributions of all other components to the heat absorption can be neglected. The heat evolved divided by the heat capacity gives the adiabatic temperature increase (i.e. without heat exchange with the environment)

T_{diff}

$$T_{diff} = 45,000 / 1,621 = 28^{\circ} \text{C} \quad (19)$$

This calculated temperature increase represents the full reaction. As we already know, approximately half of this reaction takes place during the soaking time. Some 14°C temperature increase is to be expected before the current is switched on.

Ohmic Resistance

The specific gravity between the plates is now around 1.06 (and inside around 1.02 g/ml). The conductivity of this acid is still 50% of the standard one (1.28 g/ml at 20°C), i.e. around 40 ohm⁻¹ · cm⁻¹. The maximum current density i used in plate formation will rarely exceed 25 mA/cm² (approx. 8 h charge). With double insertion and a plate clearance of $d = 7$ mm the ohmic heat losses p_{ohmic} can be estimated to:

$$\begin{aligned} P_{ohmic} &= R + i^2/d \\ &= (0.025) (0.7) (0.025^2/0.7) \\ &= 15.6 \times 10^{-6} \text{ (W/cm}^3\text{)} \\ &= 56 \times 10^{-3} \text{ (J/h} \cdot \text{cm}^3\text{)} \end{aligned} \quad (20)$$

This can be converted into a temperature increase T_{ohmic} using the electrolyte heat capacity of $0.92 \cdot 4.226 \cdot 1.06 = 4.12 \text{ J/cm}^3$.

$$T_{ohmic} = 56 \times 10^{-3} / 4.12 = 14 \times 10^{-3} \text{ }^{\circ}\text{C/h} \quad (21)$$

The ohmic loss between the plates therefore can be neglected as a heat source of significant influence in formation, even if double the current is used resulting in four times the energy losses or temperature increase (0.05°C/h).

The Ohmic resistance inside the plates cannot be calculated in simple terms due to the complicated structure. As it can be recognized only by the potential, it will be included in the polarization effects.

Polarization

The open circuit voltage at a specific gravity of 1.06 g/ml is 1.90 V. In the formation the voltage rises to 2.4 V before gassing becomes important. Simply speaking this overvoltage starts when the formation of fresh lead sulfate becomes smaller than the consumption due to conversion into charged active material.

This happens with the decrease of accessible lead oxide or basic lead sulfate. Simultaneously the specific gravity inside the plates rises. This is called polarization resulting from lack of lead sulfate. Using the same current density of 25 mA/cm² it will be 500 mV (2.4 V - 1.9 V) and the heat evolution

$$\begin{aligned} T'_{ohmic} &= U (i/d) \\ &= 0.5 (0.025/0.7) \\ &= 0.018 \text{ (W/cm}^3\text{)} \\ &= 15.6 \text{ (}^{\circ}\text{C/h)} \end{aligned} \quad (22)$$

This obviously is an enormously high rate, but it makes clear that the current at this stage must be reduced. But even at 10% of the initial current we will find a heat evolution equivalent to a temperature increase of some 1.5 degrees per hour at this voltage.

Gassing

Gassing, i.e. oxygen and/or hydrogen evolution, is the normal side reaction in the lead-acid battery. It is connected with an overvoltage, the necessary condition for the successful operation of the batteries.

The standard OCV of the hydrogen - oxygen cell is 1.23 V, while in a battery during gassing 2.6 V to 2.8 V are found. The difference is due to the kinetic inhibition and results in the equivalent heat evolution.

Using equations (22) and (21) with a current density of 10 mA · cm⁻² the resulting temperature increase is expected to be

$$\begin{aligned} &= (2.7 - 1.23) (0.01 / 0.7) \\ &= 0.021 \text{ (W/cm}^3\text{)} \\ &= 18.4 \text{ (}^{\circ}\text{C/h)} \end{aligned} \quad (23)$$

Taking into account that 10 mA · cm⁻² is approximately the 6 h rate for an automotive battery plate (depending on the thickness of course), it can be understood that not only in formation but also in normal battery charging the current

must be decreased, once the gassing voltage is reached. Other aspects besides the temperature, like shedding, might be seen as even more important, but are not part of these considerations.

2.5.2 Heat Sinks

There are two heat sinks in a plate formation. One is the heat transfer through the container walls, the other one is through the exhaust air. Since the container walls are a poor thermal conductor, only exhaust air is of real importance, so this is the one to consider.

Cooling Formula

The exhaust air under ideal conditions will flow horizontally over the electrolyte surface and absorb energy E_{air} according to

$$E_{air} = \alpha \cdot A \cdot \Delta T \quad (24)$$

with ΔT the average temperature difference between air and electrolyte, A the area of heat transfer, and the transient coefficient α , which under such conditions is approximately

$$\alpha = 6.2 + 4.2 \cdot v \cdot (J \cdot m^{-2} \cdot sec^{-1} \cdot K^{-1}) \quad (25)$$

with v the air velocity in $m \cdot sec^{-1}$ ($v < 5$ m/s). Additionally, the air will pick up moisture according to

$$E_{moist} = (\alpha / C_p) \cdot (x' - X) \cdot A \cdot E_{ev} \quad (26)$$

with C_p the heat capacity of air ($1.05 \cdot 10^3 J \cdot kg^{-1} \cdot K^{-1}$), x' and X the relative moisture contents in kg/kg of the incoming and the leaving air at their respective temperatures, and E_{ev} the energy of evaporation of water. This is

$$\begin{aligned} \text{at } 40^\circ C & \quad 2.4 \times 10^6 J \cdot kg^{-1} \\ \text{at } 60^\circ C & \quad 1.6 \times 10^6 J \cdot kg^{-1} \end{aligned}$$

Values for x' and X are

at 40° C and 100 % RH	0.051 kg/kg
at 60° C and 100 % RH	0.159 kg/kg
at 25° C and 80 % RH	0.016 kg/kg

Assuming the ambient to be 25°C and the electrolyte temperature 40°C and the air temperature rising to 40°C, the average ΔT is given as:

$$\Delta T = 0.5(40 - 25) = 7.5 \text{ [K]}$$

leading to

$$E_{air} = \alpha \cdot A \cdot 7.5 \text{ and}$$

$$E_{moist} = \alpha \cdot A \cdot 2.4 \times 10^6 \cdot (0.051 - 0.016) \cdot 1.05 \cdot 10^3$$

$$= \alpha \cdot A \cdot 80$$

The total heat transfer per area unit is then the sum

$$E_{tot}/A = \alpha \cdot (7.5 + 80) \quad (27)$$

for which we need only the air stream velocity to determine α . In order to do this, the easiest way is to use an example.

Exhaust Requirements

In a formation container with a 20 mm plate pitch p (the distance from the center of one negative groove to the next one) and a 3-fold insertion there are 3 negative panels per

20 mm cell length. With panels e.g. 148 mm wide and 22 Ah nominal capacity C_{nom} the cell width w is around 155 mm. A total charge of 150% of the theory in the time $t = 20$ h a constant current is assumed for formation. This current can be converted into a specific current i_{ar} based on the electrolyte surface area A of

$$i_{ar} = C_{nom} \cdot 2 \cdot 1.5 / (t \cdot A) \quad (28)$$

or with the actual values

$$\begin{aligned} i_{ar} &= 22 \times 3 / (20 \cdot 0.155 \cdot 0.02) \\ &= 1064 \text{ (A} \cdot \text{m}^{-2}) \end{aligned}$$

Close to the end of the formation all this current will be converted into hydrogen of the amount (see equation 13)

$$2 \text{ el-mole} = 22.4 \text{ litre } H_2 = 53.6 \text{ Ah} \quad \text{or}$$

$$1 \text{ A} = 0.4181 / hH_2 \quad (29)$$

The amount of oxygen evolved is half of this according to equation 14. In order to avoid the danger of explosion this hydrogen must be diluted down to a maximum of 2% (fact 33 including the oxygen), which gives us

Using the area specific current as calculated above give

air flow = $1064 \times 0.0138 = 14.7 \text{ m}^3 \cdot \text{h}^{-1} \cdot \text{m}^{-2}$ Assuming a cell length of 0.5 m and a slit width at the fr< access of 2 cm this results in

$$\begin{aligned} v &= (14.7 / 3600) (0.5 / 0.02) \\ &= 0.10 \text{ m} \cdot \text{sec}^{-1} \end{aligned}$$

One should provide a safety factor of 5 resulting in $v = C$ m/sec. Now with

$$\alpha = 6.2 + 4.2 \times 0.5 = 8.3$$

Cooling Power

the heat transfer can be calculated to #

$$\begin{aligned} E_{tot}/A &= 8.3(7.5 + 80) \\ &= 726 \text{ (J} \cdot \text{m}^{-2} \cdot \text{sec}^{-1}) = 726 \text{ (W} \cdot \text{m}^{-2}) \end{aligned}$$

Notwithstanding the fact that this is an ideal situation of which one might expect only some 30% in practice, the calculation shows what must be taken into account for design.

The cooling by water evaporation is by far the most important heat sink. This evaporation is only possible if the moisture saturated air is removed continuously from the electrolyte surface by careful control of the exhaust air stream.

The slit design and the positioning of the exhaust hoods are the important features to allow for short time formation (high current density) and multiple panels per groove for automotive or maximum nominal capacity per container for industrial plates.

After all, it is almost self evident that with a given production rate the area of the formation room and the sizing of the rectifier are related to the cooling efficiency to a very high extent.

2.6 Performance Aspects

2.6.1 The Electrolyte

The electrolyte is pure diluted sulfuric acid. For the acceptable level of impurities in most countries in the world standards are used, of which an example can be found in the appendix.

Specific Gravity

Electrolyte strength can be characterized in the easiest way by its specific gravity (s.g.), as this is strictly correlated to the concentration. For convenience reasons a table showing the relations is also found in the appendix. The s.g. depends on the temperature and decreases with increasing temperature according to

$$\text{s.g.}(T) = \text{s.g.}(20) - 0.0007(T - 20) \quad (30)$$

In most cases 20°C is used as base, but also 15, 25, and 30°C are found. The reference in this book is always 20°C.

Relation to Performance

The concentration of the formation electrolyte determines to a certain extent the relation between alpha and beta PbO₂ and so the electric properties of the formed plates determine the current efficiency of the positive plate formation.

In the sixties it was quite common practice for SLI batteries to use a low s.g. electrolyte of, say, 1.06 g/ml. This allowed for short formation times, down to 8 hours, with high current efficiency. Values of 300 Ah/kg dry mass gave a PbO₂ content of 92% when the starting material was a highly porous paste, referring to the status after curing and drying.

SLI Batteries

The use of low gravity electrolyte produced a high percentage of alpha PbO₂ with the disadvantage of poor cranking power. In recent years the automotive manufacturers have demanded light weight batteries with higher performance standards. This forced the battery industry to improve formation practices to meet the demand. Pressure for even further improvement continues.

The easiest way to achieve this is to increase the s.g. of the formation acid. Now, for high performance batteries, especially for high cold cranking power, a s.g. of 1.12 or even 1.15 g/ml as starting point is used. Starting point means the s.g. immediately before loading the tanks with plates.

The consequence is not only a higher percentage of beta PbO₂ but also a lower current efficiency. Some 360 Ah/kg are quite normal to get full capacity in the first discharge. Additionally the formation time must be increased otherwise the gas evolution would be enormous and the temperature rise (section 2.5) would increase the percentage of alpha PbO₂ which is contrary to the objective.

Industrial Batteries

For industrial plates of pasted type the high rate performance is not that important. Even for short duration stationary batteries are rated for 15 minutes and traction batteries are designed for around 30 minute peak rate loads and they might be delivered at a status of 95% of nominal capacity.

Remembering the glue effect of alpha PbO₂ a higher content of this will prevent shedding of the positive active material. The normal way is to operate with low porosity, i.e. low amount of sulfuric acid added to the paste, rather than low s.g. This results in a high pH in the plates for a longer period of time and so also in a high percentage of alpha PbO₂.

In tubular plates the tubes prevent shedding quite efficiently. So the beta content can be higher and efforts are made to achieve this by low apparent density of the filling material (high porosity) and fairly high specific gravity (ca. 1.15 g/ml) in formation. The initial capacity is high and lead utilization is much better than in pasted plates.

Specific Gravity Control

Whenever the plates are taken out of the tanks they include quite a large volume of electrolyte, so the tanks must be refilled for the next batch.

During formation the acid used to make the paste is released and some water is lost due to gas evolution. So the concentration at the end will be higher than at the beginning. No general rules can be given to what extent this will happen since it depends on the relation between active material and total electrolyte volume, the active mass recipe (content of SO₃), and the amount of overcharge.

Therefore the refilling acid must be much more diluted than nominal and in many cases it can be deionized water only. Most battery manufacturers have a diluted acid with a concentration meeting the average demand stored in high tanks. Hoses with a pistol grip and shut off valve are used for refilling tanks.

A variance of 0.02 g/ml with respect to the nominal s.g. can be tolerated at maximum. Otherwise the performance might differ for different formation batches.

2.6.2 The Dry Charge Problem

Plates, if properly made are at the peak of performance immediately after formation and should then be used to make dry charged batteries. The electrolyte must first be removed. This is done by washing and drying.

The plates are either hanged or stacked into rinsing tanks with tap water. It is neither possible nor recommended to remove the last traces of sulfuric acid. In the positive plates some residual acid prevents, to some extent, a reaction between the PbO₂ on the grid (corrosion layer) with the metallic lead from forming insulating lead oxide PbO. In the negative plates it hampers the oxidation by air of the spongy lead.

The real problem is the drying. The plates should be very dry. With more than 2% residual moisture the capacity loss during storage in most cases is not acceptable.

Plate Drying

Positive plates normally are dried in tunnel type ovens operated at fairly high temperature. The evaporating water keeps the plates cool. Nevertheless some reaction at the grid surface is unavoidable leading to a lower performance after drying.

The extent to which this happens depends mostly on the residual acid content and the degree of overdrying. Tests with the DIGATRON/FCI Single Plate Tester comparing the capacity before and after washing and drying give an indication of this and are often used in quality control. More details are given in the appendix.

Negative plates would reoxidize during drying in air. So drying is made under protection. Three ways are quite common,

- vacuum
- hot plate
- inert gas

of which the last one seems to be the most reliable and least expensive. The "pommes frites" method, boiling in kerosene, has proven to be too dangerous.

The spongy lead in the negative plates may recrystallize during the drying process at elevated temperature leading to a coarser structure with less activity and lower high rate capacity. As with the positive plates comparative capacity tests are recommended to adjust the production parameters properly.

3. Container Formation

Formation of plates that have been cured, dried and assembled into groups can be done in the container in which they will operate. This method is also called jar formation.

The chemical and electrochemical reactions in container formation are the same as in plate formation. So reference is made to chapter 2 for details and only the differences will be pointed out here.

3.1 Principal Advantages

Whatever aspect one might consider, container formation shows advantages. Investments for equipment including maintenance, scrap rate, direct labor, and environmental control efforts can be reduced significantly. Additionally, in many cases the product quality can be improved.

Most importantly, a number of very difficult, expensive and environmentally unpleasant operations are eliminated. Without forming tanks there is less formation gas to control, less acid on the formation floor and no lead sediment or dusty lug brushing operations that have to be vented, filtered, etc.

The elimination of these operations results in a reduced capital investment requirement and a rather large savings in direct labor.

As almost each working place in the lead-acid industry requires its own exhaust with respective filter and filter cleaning, the reduction of working places reduces this problem automatically. Further improvements are achieved due to less acid and acidic water waste which must be neutralized and filtered as well as dumping of sludge.

There is always some sediment of active material in the formation tanks, which must be removed from time to time, as it will otherwise lead to shorts. This task and the sludge recycling is eliminated.

Finally, the quality of the product can be improved. There is no danger of grid - active material interaction in the

positive plates (thermopassivation) or decomposition of organic expanders in the negative plates. This improves service life and the performance of SLI batteries to a noticeable extent.

With all these advantages there must also be some disadvantage. These are the temperature and the electrolyte problems and the limited shelf life of activated batteries.

3.2 Shelf Life

The shelf life is not a problem in most cases for industrial batteries, as they are produced on order. Whether the manufacturer keeps a plate or a cell inventory does not make a significant difference in this respect. More details are discussed in application.

The automotive battery production is different by its nature. The batteries are produced in batches either for intermediate storage in warehouses or for original equipment (O.E.) in new cars.

In O.E. battery production storage must be taken into account. It might require up to six months (and in some cases even more) for a car from assembly to final delivery to the end user. During this time the battery is not charged all, but rather discharged through the small power consumers, like the clock, leakage currents, and on-board computers. Some cranking is required for intermediate transport such as on and off the truck, train, ship and on the dealer yard.

Taking all these items into consideration and adding the self discharge, this treatment is not in accordance with textbooks on lead-acid batteries. Nevertheless O.E. batteries live some 5 to 7 years in the U.S.A. and Europe and a 3 year guarantee is quite common.

The storage problem was solved with the development what is called a maintenance-free battery. In these batteries the grids are cast in low antimony alloy with around 2% or less Sb or with antimony free Pb-Ca alloys. Expanded metal is used by some manufacturers.

The different solutions will not be discussed here, only the effect on storage behavior. With low antimony the self discharge rate is reduced and together with accurate regulators, in the cars refilling with water is no longer necessary during service life. The consequence of this is extended shelf life, which nowadays can be 9 or even 12 months.

With such shelf life and reasonable stock policies there is no further reason to produce replacement batteries as discharged.

3.3 Acid Concentration

In ideal container formation the electrolyte at the end of the charge meets the specifications for specific gravity and level. This is standard in automotive battery production, as will be worked out in 4.1, while industrial batteries in some cases are charged after a replacement of the electrolyte (two shot process), or acid adjusted if a one shot process.

A reason for using a two shot process is the difference in the specific electrolyte volume per unit of active material. This leads to a higher difference in concentration of the acid between filling and after soaking. Also, the acid

concentration is higher after charging than the concentration after filling.

The thin plates in automotive batteries are not affected to the same extent by these differences as are the thicker industrial plates and so more compromises are unavoidable.

3.4 Temperature

The limited acid also leads to more severe temperature problems in container formation during the soaking period. The heat insulating containers make the situation even worse. So the rest period between filling and start of charge is no longer determined by the necessary soaking time but by the heat dissipation.

Further heat is evolved due to polarization, as we have seen before. Contrary to the neutralization energy this can be kept under control by limitation of the charge intensity by current reduction or, if possible, by voltage control.

The heat generation problem usually dictates a short soaking period with automotive batteries of less than thirty minutes.

All in all it is primarily the temperature problems which lead to charging limitations and so in general, longer formation times. Container formation therefore requires careful process control.

Reduced formation time can be enhanced by the use of chilled acid when filling (<10° C). Formation schedules with multiple charge rates can effectively control battery temperature during the forming process. The addition of forced air cooling while charging will usually allow higher charging rates than possible by normal convection cooling. The combined effects of chilled acid, programmed formation and forced air cooling can lead to significantly shorter formation periods.

3.5 Power Supply

The total DC power requirements depend on the production volume and so are the same for plate and container formation. It is the number of formation circuits which makes the main difference on the equipment side.

Tank Forming

To illustrate charging equipment requirement differences between tank and container formation, the following automotive formation is taken as an example. With $m = 40$ tanks in series ($40 \times 3 \text{ V} = 120 \text{ V}$) and $n = 52$ positive (and 54 negative) panels in a 53 groove tank and a capacity of $C_{nom} = 11 \text{ Ah}$ per plate the nominal energy E_{p1} of one formation batch is

$$E_{p1} = (2 * n * C_{nom}) * V * 10^{-3}$$

$$E_{p1} = (2) (52) (11) (40) (3) (10^{-3})$$

$$= 137.28 \text{ kWh}$$

Container Forming

In container formation 18 batteries can be set up in series ($18 \times 6 \times 3 = 324 \text{ V}$) and with an average capacity of 60 Ah the nominal energy is calculated to

$$E_{con} = (60) (18) (6) (3) (10^{-3}) = 19.44 \text{ kWh}$$

Eight container formation charging circuits are required to equal the production of the single tank forming circuit. The

above calculation is made under the provision that the formation times are the same for both methods, which is quite optimistic for container formation, as was shown with the temperature problems.

Also, the total energy required for either method is a function of current rates during the multiple phases of formation. The examples given are only intended to illustrate the relative number of charging circuits required for container formation compared to tank forming.

The situation is not that different in capacities with industrial batteries, but additionally longer formation is required. So in any case the number of circuits in container formation is much higher and with this the organization becomes more complex.

3.6 BAFOS

To handle this complex organization the DIGATRON/FCI BAFOS or MicroForm systems give a reliable hand. All circuits are provided with a microprocessor, which can store many programs simultaneously. Additionally they have memory to store all information about an actual formation batch, which is required for QC or R&D purposes.

Hundreds of circuits can be linked with a central PC by a party line, where:

- all programs are prepared and called up
- a survey is given on the status of all circuits with indication of residual running time
- programs are transferred to the single circuits for execution
- formations are started and stopped separately or in groups
- data files are set up and may be printed out as tables or graphs for each formation circuit

Examples showing how simple the operation is will be given in the application chapters.

4. AUTOMOTIVE APPLICATIONS

4.1 Plate Formation

4.1.1 General

Tank Forming Procedures

Except for the inverse initial charge and discharge the programs can be the same for traditional and tackless formation. The most convenient way is to do the formation in 24 hour cycles including the insertion and removal of the panels and topping up of the tanks. This allows for approximately 21 to 22 hours charge time.

In tackless formatieB-firer the formation tanks must be topped up, in most cases with deionized water, depending on the actual conditions, but possibly with low specific gravity acid. The acid level should be adjusted so the lugs will be completely covered.

The electrolyte can now be mixed by charging the bars with 80 to 100 Amps for some minutes. This current is reduced to 5 to 10 Amps before the plate insertion starts, first with the negative and then the positive panels. The orientation of the lugs alters with each formation (see 2.3). It is essential that the panels are allowed to fall onto the bars for the last 10 to 15 cm to give good contact.

In traditional formation leveling of electrolyte is made after panel mounting and tacking. It is always set up according to the polarity of the cables, positive plates with the lugs to the positive end and negative plates the other way. Again, first the negative and then all positive plates are mounted. Then the connections are tacked and the electrolyte topped up at least 3 mm above the top panel edge.

The formation should be switched on immediately when the set up is finalized. The thin automotive plates do not require more soaking time.

The typical formation charge is 320 Ah/kg dry positive active material. It might go up to 360 Ah/kg or even higher with poor quality oxide or poor curing (cracks, residual metallic lead >2%). Without special precautions, as will be shown in 4.1.2, it does not pay to reduce the total charge in plate formations below the 320 Ah/kg, for lack of performance after activation may result from this.

4.1.2 Practical Examples

The following example for a 20-hour formation is based on a 53 groove tank, mounted with two panels each, i.e. 54 negative and 52 positive panels, as the standard set up in the tank always starts and ends with negative panels. If each positive panel includes 180 g dry active material, the total is 9.36 kg per tank. The total charge then should be 320 x 9.36 = 2995 Ah.

In BAFOS notation the respective program is given in table four. The program steps are automatically inserted by the PC. The operator tells the rectifier what to do. DCH stands for discharge, CHA for charge and PAD for pause. The nominal values in this case only define the currents. The Switch gives the conditions, when to switch to the next step. Break indicates that under the defined conditions, if anything goes wrong the formation should be stopped. For example, a bad connection may be the reason for excessively high voltage. Registration indicates when to read and store data for later examination.

Table 4. Example of a Tank Formation Program

PS	Operator	Nominal	Switch	Break	Registration
1	DCH	100A	1:00 H	<-150V	0:30 H
2	CHA	200 A	>0V		
3	CHA	130A	0:30 H	>150V	
4	CHA	180A	10:00 H		2:00 H
5	PAU		0:30 H		
6	CHA	180A	4:00 H		2:00 H
7	PAU		0:30 H		
8	CHA	89 A	4:30 H		1:00 H
9	STO				

Due to low efficiency in the first step and to lack of acid in the plates the second step normally lasts for only 2 to 5 minutes so the total formation time is around 21 hours. For a traditional formation these two steps are excluded. The charge in steps 3 to 9 is 2986 Ah or 319 Ah/kg.

The notation shown followed the traditional way of defining a time/current controlled process and not an amphour/ voltage control, which really should be achieved. This is done in a slightly varied schedule according to table 5.

The switch conditions in the essential charging periods altered to amhours and in step 6 a voltage limitation is included, which results in a tapering down of the current z soon as 106 V (= 2.65 V per cell) is reached. With this th gassing is limited. It is well known that with this method tl current efficiency is increased and step 7 can be omitted and 8 reduced or modified.

In formation the temperature should also be limited and popular value is a maximum of 55° C.

Table 5. Modified Example for Tank Formation

PS	Operator	Nominal	Switch	Break	Registration
1	DCH	100A	1:00 H	<-150V	0:30 H
2	CHA	200 A	<0V		
3	CHA	130A	65 AH	>150V	
4	CHA	180A	1800 AH		2:00 H
5	PAU		0:30 H		
6	CHA	180A	720 AH		2:00 H
		106V			
7	PAU		0:30 H		
8	CHA	89 A	4:30 H		1:00 H
9	STO				

Including this condition in the program allows for omitting pauses and then the program becomes very simple as pe table 6 assuming some efficiency increase as indicated above.

Table 6. Simplified Example for Tank Formation

PS	Operator	Nominal	Switch	Break	Registration
1	DCH	100A	1:00 H	<-150V	0:30 H
2	CHA	200 A	>0V		
3	CHA	130A	0:30 H	>150V	
4	CHA	180A	2800 AH		2:00 H
		106 A			
		55 C			
5	STO				

Steps 1 and 2 are specific for tackless formation and th« values identical for all types of plates. Step 3 is assumed an initial low charge value to overcome the grid/active material interface problem and discharge the rest of the inverse step.

So the first significant formation step is No. 4 and for th« different plate types only the current and the amhours ar to be adjusted accordingly, i.e. assuring to charge the pan with 300 Ah/kg dry material in this step.

Again, for traditional formation only, steps 1 and 2 are omitted, while No. 3 should remain as a constant line.

One might even go further and insert the nominal value the rectifier for the nominal charging current, i.e. 250 amp; as all important parameters, voltage, temperature, and tot charge are controlled separately. There is no risk to it, if il made certain any defects in the equipment are recognizec

The rectifiers check themselves for accuracy of current and voltage. It is only the temperature probe, which might have been forgotten to be inserted (lack of connection gives reading -273°C.). So we must break the program in such case and transmit an alarm.

Even in cold winter days the electrolyte temperature will never be less than 40° C in moderate climates. This leads to the program in table 7, where only the underlined value for the charge amount must be adapted to the type of plates.

Table 7. Safe but Simple Example for Tank Formation

<u>PS</u>	<u>Operator</u>	<u>Nominal</u>	<u>Switch</u>	<u>Break</u>	<u>Registration</u>
1	DCH	100A	1:00 H	<-150V	0:30 H
2	CHA	200 A	>0V		
3	CHA	130A	0:30 H	<40V	
4	CHA	250A	2800 AH	<40V	2:00 H
		106 A			
		55 C			
5	STO				

4.2 Container Formation

4.2.1 General Procedures (one shot)

The principles for container formation of automotive batteries were discussed in chapter 3. There are limited options for variation of the specific gravity of the filling electrolyte for the purpose of achieving optimum formation results.

It is around 1.24 to 1.25 g/ml depending on the actual paste recipe used. The exact value is to be adjusted so that after full charge the battery acid will have the nominal concentration, i.e. 1.28 g/ml in most cases.

With the high specific gravity filling electrolyte the neutralization reaction becomes quite vigorous leading to a peak temperature exceeding 70° C. With normal convection cooling of table or conveyer formation, the heat insulating characteristics of polypropylene containers make it necessary to allow for a cooling period. The time necessary to load tables or conveyers and electrically interconnect batteries can be sufficient to allow charging to start. Cooling calculations are difficult and rarely give satisfying results.

After charging, the batteries require leveling of the electrolyte. This is primarily due to the fact that the batteries are normally not filled to the correct level the first time to allow for gassing and secondly to make up for the water losses during charging. The leveling should be possible with standard operating acid, i.e. specific gravity 1.28 g/ml.

The vent plugs are now mounted and the batteries washed free of acid. Finally, they should be checked for correct specific gravity by reading their OCV. This is then followed by a high rate load performance test utilizing a two to five sec high current discharge pulse and reading the respective voltage underload. Both tests are made simultaneously by automatic test equipment in most factories and include rejecting of faulty batteries. For more information see the brochure on the DIGATRON/FCI Production Line Tester PLT.

4.2.2 Formation Set Up

After the fully assembled batteries are filled with acid in an automatic filling station there are two principle ways of further handling dependent on the type of battery transport system. The batteries may be stacked on pallets and brought to the formation room by fork lift trucks or moved on roller conveyers.

Figure 12 shows a schematic layout of a container formation with roller conveyers. It is feasible only if assembly lines, formation and final assembly are set up as one block. The investment cost is high, as the construction materials must be acid resistant (stainless steel, PVC), but the actual transport costs are low. Forced air cooling of batteries on conveyers is far more practical than with other methods.

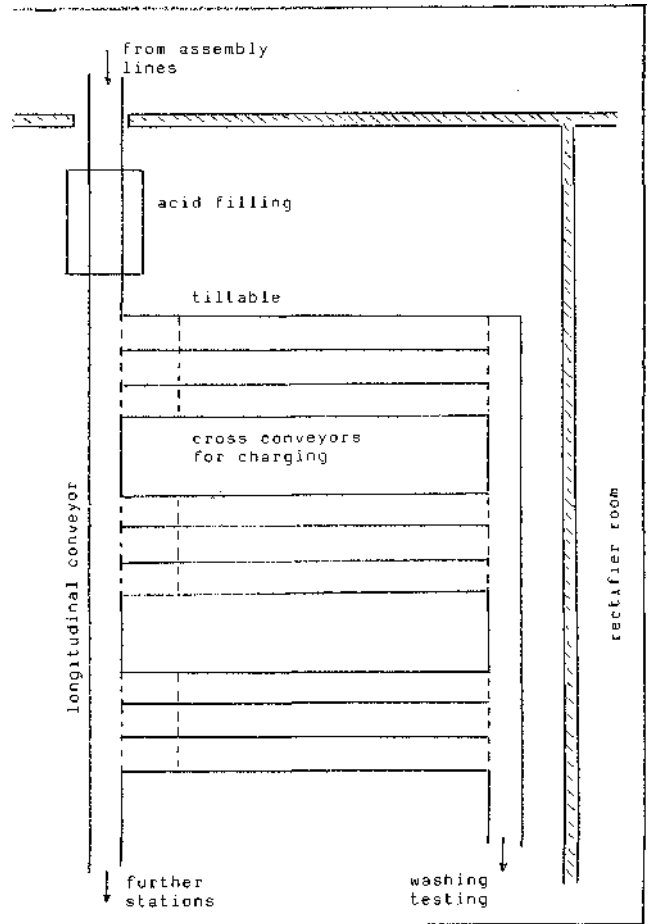


Figure 12. SLI Container Formation Layout with Roller Conveyors

Figure 13 shows the layout for a pallet/fork lift transport method. The investment is low, but more space is required and more direct labor is involved. Assembly and formation need not be adjacent. Cooling is possible both with air and with water, but with greater environmental concerns and less effectiveness.

Cooling of the batteries allows for shorter formation time and so provides better utilization of the total facility. On the other hand additional investment is required.

Water cooling is made by replacing the stands in figure 13 by water baths also using neutralized effluent water as the cooling medium. The cooling water will absorb a good part of the acid fumes created during charge so must again be neutralized and recycled. Since the water does absorb significant acid fumes, the requirements for exhausting the ambient air can be reduced.

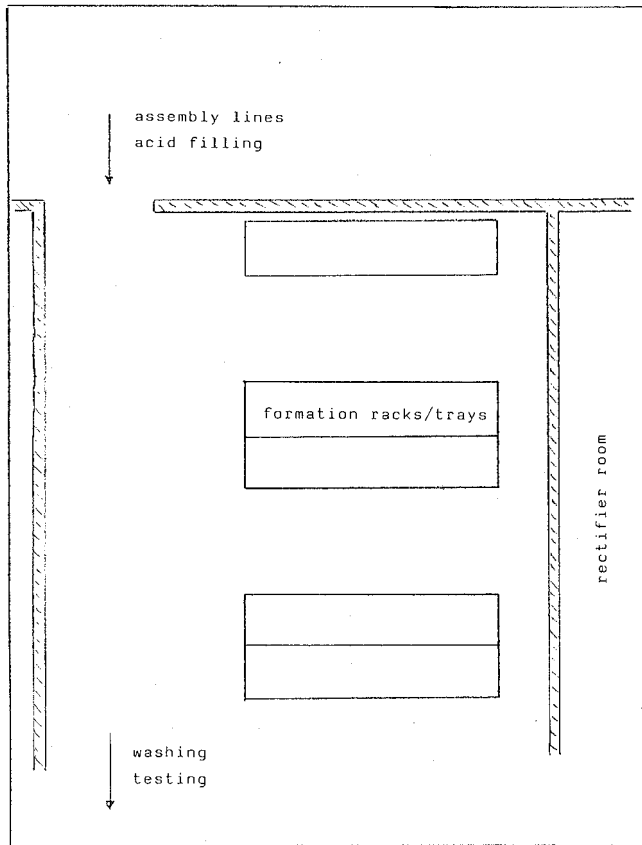


Figure 13. SLI Container Formation Layout for Pallet Handling

Air cooling requires a substantial quantity of moving air along the sides of the batteries. This may be done in several ways. Recent approaches have included ducted air alongside of or from beneath conveyers. It is not important that the air be cool, only that it is moving at a velocity that effectively reduces surface temperature of the batteries effectively.

Normally, interconnection of batteries is made by cables with cast on lead rings which fit on battery terminal posts. Spring type copper bronze straps are also used. They are reasonably acid resistant and ensure good electrical contact by a partial circle cut-out at their ends. All connector types must be cleaned or changed frequently to avoid arcing at battery post connections.

4.2.3 Traditional Formation Programs

For a better understanding of the optimization of formation, one should look at the somewhat contradictory objectives.

- high quality (performance, service life)
- short duration (performance, service life)
- low energy consumption (energy costs, temperature)
- low environmental problems (corroding acid fumes, problems, overformation, neutralization)

Each of these points is related to specific costs. Minimizing the total cost is a must for automotive batteries. The first problem encountered is the initial temperature rise after acid filling. Chilled acid is sometimes used in

specific situations but in general is not cost effective. Therefore, a cool down period should be considered. The diagram figure 14 shows the initial temperature rise and the following cooling phase for a 72 Ah automotive battery.

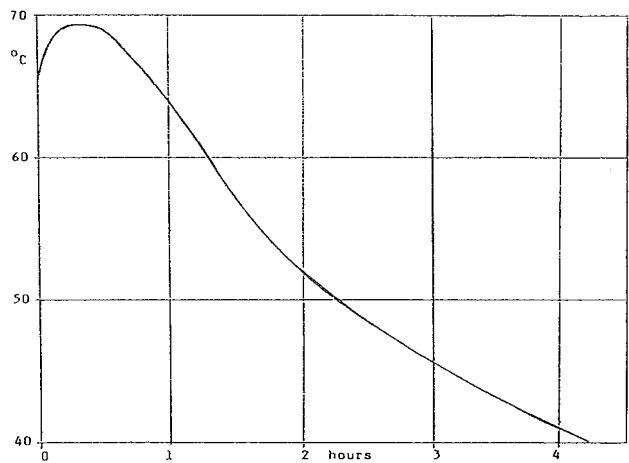


Figure 14. SLI Battery Temperature after Filling for Container Formation

Assuming that shortly after the culmination point the neutralization reaction is nearing completion, the exponential decrease leads to a time constant according to

$$temp_{act} = temp_{max} * \exp(-t/\tau)$$

which in this case is 5.1 h. It will be different but similar for other types and sizes and gives us an idea about the time base for the design of a formation program.

The following illustrates progressive enhancements of formation charging using BAFOS or MicroForm programmed formation control.

Starting very simply we allow for cooling under an operator's supervision and give an indication to start charging once the batteries are cooled down to 50° C. To make sure that no temperature problems will arise later on we go for a 2 day cycle allowing for 44 h charging time. This leads to table 8.

Table 8. Simple Container Formation Program for 12 Batteries 72 Ah

PS	Operator	Nominal	Switch	Break	Registration
1	CHA	3.6A	0:15 H	>216V	
2	PAU		2:45 H		
3	CHA	7.2A	4:00 H	>150V	1:00 H
4	CHA	9.0A	10:00 H		2:00 H
5	PAU		0:30 H		
6	CHA	5.4A	16:00 H		2:00 H
7	PAU		0:30 H		
8	CHA	3.6A	10:00 H		1:00 H
9	STO				

In the first step the operator checks the circuits, which are started at one time to see that connections are made properly. This can be confirmed by a manual voltage reading or by reviewing voltage data at the computer. This is followed by the cooling phase step 2.

In the initial stage of the formation the charge current will create more heat inside the plates. There are Ohmic losses under low conductivity conditions of the electrolyte and the grid-active material interface leading to high battery voltages. Furthermore we have the continuing neutralization reaction to lead sulfate. In step 3 the charge current is fairly low at 10% of the capacity.

The electrolyte specific gravity increases significantly only after approximately half of the active material is converted electrochemically into PbO₂ and Pb respectively. This is equivalent to a charge of the nominal 20 h capacity.

Before this point is reached we know that the voltage decreases and so the current can be increased as in step 4 to 12.5% of C₂₀ until the voltage rises again.

High polarization and gas evolution are the main heat sources from now on. So a little pause allows for some cooling down (step 5) before charge is continued with a smaller current (step 6) of 7.5% of C₂₀, for 16 hours.

After a further short pause the charge is finished with a low current of 5% of C₂₀, which will not do any harm with almost 100% conversion of the current into gas.

During a total duration of 44 h the batteries are charged with 241.2 Ah or 3.35 «C₂₀. Assuming a design with 50% mass utilization at the 20 h rate this is equivalent to 167.5% of the theoretically required charge.

With the knowledge about BAFOS and MicroForm computer control from chapter 4.1, one may see the advantages such a system brings into the formation room. The cooling phase no longer needs to be a fixed time as in program card controlled chargers (see 2.4), and undefined waiting periods can be used by introducing a command to wait until the battery temperature is, for example, below 50°C.

The visual check of the circuit by an attendant can be excluded with reliable interbattery connectors and check of the actual voltage on the computer screen. This leads to the program in table 9.

Table 9. Improved Container Formation Program for 12 Batteries 72 Ah

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<50 C		
2	CHA	7.2A	4:00 H	>216V	1:00 H
3	CHA	9.0A	10:00 H		2:00 H
4	PAU		0:30 H		
5	CHA	5.4A	16:00 H		2:00 H
6	PAU		0:30 H		
7	CHA	3.6A	10:00 H		1:00 H
8	STO				

With the assistance of BAFOS or MicroForm, a schedule can be developed that will optimize time and energy usage. The program can easily be modified to compensate for seasonal temperature variations.

Depending on ambient conditions, the currents indicated in steps 2, 3, 5 and 7 may be increased by as much as 25% allowing completion of formation in approximately 24 hours.

4.2.4 Temperature Controlled Formation

A general scheme for container formation of automotive batteries should include

- control of electrolyte temperature to avoid damage
- maximum allowable current level to keep total time short
- low acid pollution of the environment
- low energy consumption

Such aspects are difficult to realize with manual and timer controls, but easy to accomplish with BAFOS or MicroForm computer control. These systems provide programmed control of electrolyte temperature, battery voltage, formation current, and total charge in amphotours as process controlling parameters in multistep formation programs.

In figure 15 the initial two hours of a formation using temperature control are shown. The maximum current was

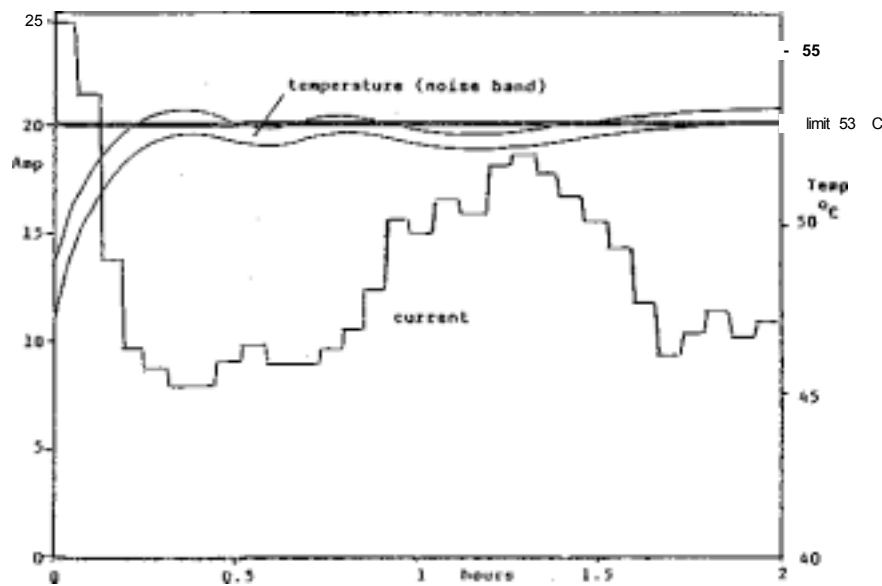


Figure 15. Temperature Controlled Formation Initial Battery Behavior

set to 25 A and the electrolyte temperature was limited to 53°C. With high current the temperature rise is quite steep at three degrees below the maximum temperature current is reduced in order to avoid exceeding the limit.

As expected, after some 45 minutes the heat evolution became smaller and therefore allowed current to increase. This period lasted for 40 minutes before the current had to again be reduced.

An unrealistically low temperature limit was used in figure 15 for demonstration of formation by temperature control. A more realistic example for container formation of automotive batteries is given in table 10 for a 72 ampour battery. The results for this formation are given in figure 16.

Table 10. Improved Container Formation Program for 12

Batteries 72 Ah					
PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<50 C		
2	CHA	25A 60C 192V	155 ah	>216V	1:00 H
3	CHA	187.2V	3.6A		2:00H
4	CHA	3.6A	180 AH		1:00H
5	STO				

The initial pause (PAD) allows for a cooling down to 50°C before a maximum charge (CHA) current of 25A is applied. Thereafter, a temperature of 60°C and a voltage of 16 V should not be exceeded. After a total charge of 155 Ah the further charge will be limited to a voltage of 15.6 V per battery until the current is reduced to 3.6 A.

Then the battery normally is fully charged. Just in case anything goes wrong such as an inter-battery connection creating a significant voltage drop, a third step makes sure that with a constant current the battery is charged up to the necessary 180 Ah, i.e. 2.5 times the nominal capacity.

According to figure 16 the high initial current in an experiment could be kept only for 30 minutes before the rising temperature made a reduction necessary. This information can be used to open a cooling water valve or start a fan for forced air cooling if such facilities are utilized.

After 3.5 hours, the programmed control increased current from 15 to 20 A. With this increase, voltage and the Ohmic losses rose causing temperature to reach the programmed limit in seven hours which further resulted in a decrease of charging current.

After 8 hours the maximum voltage of 16 V (2.67 V/C) was reached. At this point, current tapered down until after 13.5 hours 155 Ah were charged and the program switched to a constant voltage charge at 15.6 V per.battery.

This step lasted 23 hours with almost constant current and the total charge actually reached 185 Ah. The third step was not used in this case.

A capacity test with the 20 h rate (3.6 A) showed 69 Ah or 96% of the nominal value. After excessive recharge it was improved to 71 Ah and using the extended program similar to table 8 only 70 Ah were reached with sample batteries from the same production batch.

This example demonstrates that with standard automotive

batteries from normal production it is possible to perform a container formation in less than 24 hours using a current amount of only 2.5 x C₂₀ or some 120% of the theoretical value. The time savings result from the optimum utilization of the charge acceptance of the batteries and the temperature reduction achieved by programmed voltage limitation

General Program

The program in table 10 can also be used as a general base for any other type of automotive battery, provided the conditions described in the introduction are observed. The rules are as follows:

- in step 2 the nominal current is limited to the charger rating
- for all types the acceptable temperature limit is the same, with the actual value adapted to the specifics of production generally 55° C to 60° C is used and

- the switch condition in step 2 is set to the correct relay to the capacity, i.e. $2.15 \cdot C_{20}A$

- the nominal current in step 3 is $0.05 \cdot C_{20} A$

- the nominal current in step 4 is set to $0.05 \cdot C_{20} A$ and the switch condition to $2.5 \cdot C_{20}$ The

above criteria will achieve:

- low energy consumption
- low evolution of acid fumes
- highest utilization of charger output rating Additional benefits realized will include saving floor space and reducing corrosion problems in the formation area due to limited gas evolution.

Under higher ambient temperature conditions the proposed program may not work as well and a 24 h cycle may not be achieved. Then there are two options. First is the introduction of additional cooling as described in 4.2.2. The second option is to increase the positive active material to improve the charge acceptance in amperes and ampour which works. Simultaneously, the overcharge with respect to the theoretical amount may be reduced.

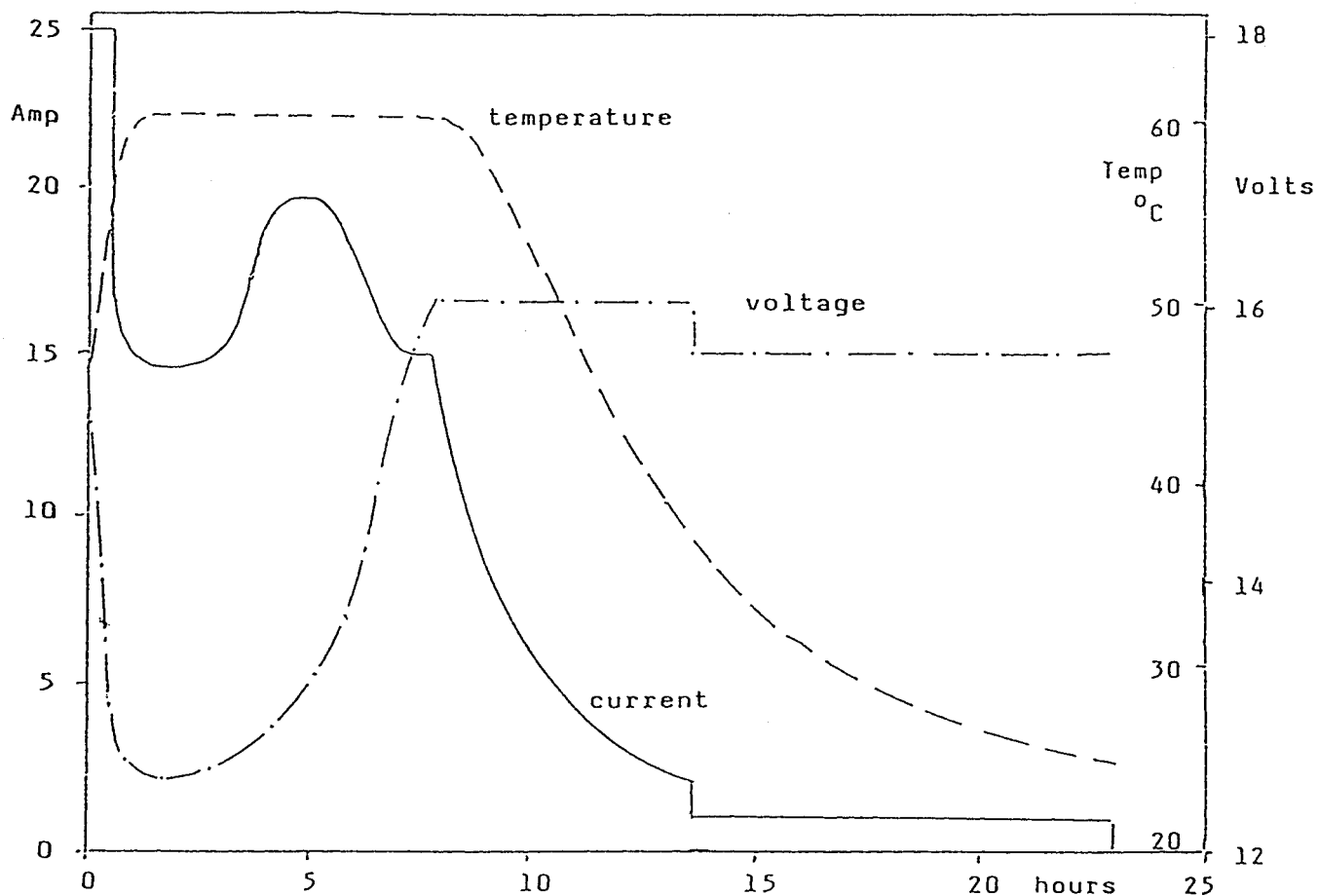
Considering the first proposal of no cooling, low cost ventilation, 24 h cycle time, properly sized chargers and small space requirements it may well pay to include some 10% more active material in the positive plates. The foregoing shows the way for formation optimization although further work may be required for specific battery designs and types. The result will also depend on the priorities, such as cold cranking, reserve capacity or 20 h capacity.

5. INDUSTRIAL APPLICATIONS

5.1 Specifics of Industrial Batteries

The variety of designs in industrial batteries is much more extensive than in automotive. Three essentially different positive plates are made:

- Plante type (large surface cast lead, active material formed from this lead)
- Faure type (pasted plates, thicker than automotive)
- Tubular type (comb style grids, covered with porous tubes and the intermediate space filled with active material)



Today, all negative plates are of the pasted type, and in spite of larger dimensions the main difference to the automotive plate may be different expanders. This presentation will deal with pasted and tubular plate batteries only.

Red Lead

While the use of red lead in automotive positive plates is rather a rare case, it is still quite popular in industrial plates.

Red lead by reaction with sulfuric acid is decomposed to lead sulfate and beta PbO_2 . Pure red lead therefore is a suitable filling material for tubular plates. In pasted plates it would lead to early shedding and therefore it is blended with lead oxide powder.

Tubular Plates

The filling material for tubular plates in practice is varied from pure lead oxide to pure red lead. Pure oxide is recommended for traction batteries only, since it is difficult to obtain full performance at the beginning, which is generally not acceptable for customers of stand-by batteries.

Pure red lead allows formation times as short as a 24 h cycle, but it is more costly. A measurable benefit starts with a blend containing at least 7% red lead. Popular values are 25% or 40%. With blends, a discharge and charge cycle will formation is used in many factories for stationary batteries.

The need for curing, which provides a good contact between spines and active material, is often underestimated in tubular plate production.

Pasted Plates

Similar paste compositions used in automotive batteries are quite popular for pasted positive plates. Traditionally, the sulfuric acid content is significantly smaller to give a higher density which results in a more rigid plate with a higher proportion of the alpha PbO_2 .

Red lead is blended into the oxide by many manufacturers in an amount of 7% to 15% to improve the conversion efficiency in formation and the resulting performance. Then a reduction of sulfuric acid concentration is required in the paste mixing formula.

Traction batteries are often shipped with only 80-85% of their nominal capacity. Under this condition red lead is not required. The positive plates for stationary batteries must be discharged and charged two or more times for full performance if red lead is not added to the paste.

Taking into account all the variations, it should be understood that only examples can be given for industrial plate and container formation.

5.2 Plate Formation (Tank)

The following examples of industrial container formation can be given:

The first example deals with tubular plates filled with 100% red lead. According to the formula PbC^{\wedge} red lead should have

PbO_2 Content = $(100)(239) / (2 \times 223 + 239) = 34.9\%$ In practice it is much lower. A quite commonly used quality is around 27% and for best quality around 32% PbO_2 . With the first type the theoretical formation charge based on dry filling weight is

$f_{th} = (2)(26.8)(730)/223 = 175.5$ Ah/kg Assuming a filling weight of 12.5 g per nominal ampour capacity C_{nom} and a formation charge of 150% of the theoretical value, this leads to 3.3 C_{nom} . A 20 h formation may then be achieved for Red Lead Filled Tubular Plates.

Table 11. Plate Formation Program (40 tanks) for Red Lead Filled Tubular Plates

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<35C		
2	CHA	0.15C	4:00H	>112V	1:00 H
3	CHA	0.25C	6:00H		2:00 H
4	PAU		0:30H		
5	CHA	0.15C	7:00H		2:00H
6	PAU		0:30H		
7	CHA	0.075C	2:00H		1:00H
8	STO				

In this table the nominal values are given as portions of the nominal capacity, i.e. 0.15 means $0.15 \cdot C_{nom}$ amps., and to be multiplied with the number n of positive plates per formation tank. The pauses are needed in order to allow for the electrolyte temperature to settle down. The different currents are a poor reflection of the charge acceptance. With BAFOS this can be directly controlled.

With $n = 24$ and $C_{nom} = Ah$, a BAFOS program would be less complex and with respect to the temperature independent of the ambient temperature (table 12). A further advantage is the ampour control and limited gassing. It can be expected that savings in the total charge requirements are possible, but this is not included in the discussion.

The initial low charging current is introduced for check of proper connections only. If it is omitted the charge in step 3 should be extended accordingly.

Table 12. BAFOS Plate Formation Program (40 tanks) for Red Lead Filled Tubular Plates

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<35C		
2	CHA	360A	0:30H	>112V	0:15 H
3	CHA	600A	4800 AH		2:00 H
		72V			
		40C			
4	PAU	360A	3040 AH		2:00 H
		83V			
		40C			
5	STO				

The second example deals with a filling mixture of 25% red lead (32% PbO_2) and 75% lead oxide (25% metallic lead) for tubular plates. The total charge is to be increase first due to less PbO_2 in the mix and secondly due to low conversion efficiency. With the reduction of residual meta lead to 5% during curing the theoretical charge is

$$f_{th} = 26.8 [2(0.25 \times 0.68 + 0.75 \times 0.93)1000/223 + 4 \times 0.05 \times 1,000/207] = 234.4 \text{ Ah/kg}$$

based on the dry filling weight.

With filling 12.7 g/Ah the theoretical charge would be $ch_{th} = (234.4)(12.7/1000) = 2.98 \cdot C_{nom}$ Using a total charge of 200% of the theoretical value and same method of notation as in table 11, a reasonable formation program is shown in table 13.

The program in general follows the same rules as above. An additional option is to include discharge and recharge steps which assure high performance is achieved with the plates. For traction battery applications it can be omitted without any further problems but will result in a capacity slightly below the optimum one.

Table 13. Plate Formation Program (40 tanks) for Red Lead / Lead Oxide Filled Tubular Plates

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<35C		
2	CHA	0.15C	2:00H	>112V	1:00 H
3	CHA	0.15C	23:00H		2:00 H
4	PAU		0:30H		
5	CHA	0.125C	16:00H		2:00H
6	PAU		0:30H		
7	CHA	0.10C	2:30H		1:00H
8	DCH	0.05C	72V		2:00H
9	CHA	0.15C	6:30H		2:00H
10	CHA	0.10C	5:00H		2:00H
11	CHA	0.05C	5:00H		1:00H
12	STO				

With lower charge acceptance, the formation current should be lower over the total time compared with red lead filling. Therefore, a conversion into a BAFOS program is even less complex as shown in table 14 using again 24 plates 100 Ah each per tank.

Table 14. BAFOS Plate Formation Program (40 tanks) for Red Lead / Lead Oxide Filled Tubular Plates

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<35C		
2	CHA	360A	0:30H	>112V	0:15 H
3	CHA	360A	14400 AH		2:00 H
		83V			
		40C			
4	DCH	120A	72 V		2:00 H
5	CHA	360V	4150 AH		2:00 H
		83V			
		40C			
6	STO				

Pasted (or flat) positive plates normally are designed with more active material than tubular ones. Modern stationary plates after curing and drying contain 14.5 to 15.5 g/Ah₁₀, while traction cells may have up to 18 g/Ah₅. Compared with automotive plates, these plates are thick and so require lower specific current and therefore more time for formation.

A typical 48 h program for stationary plates with 15 g/Ah positive active material and a weight specific charge of 360 Ah/kg is given in table 15 in a current/time control version.

Table 15. Formation of Stationary Flat Plates

AM 15 g/Ah, Ch 360 Ah/kg = (5.4 C₁₀)

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<35C		
2	CHA	0.15C	2:00H	>112V	1:00 H
3	CHA	0.10C	5:00H		2:00 H
4	CHA	0.15C	8:00H		2:00H
5	CHA	0.20C	7:00H		2:00H
6	CHA	0.125C	10:00H		2:00H
7	PAU		1:00H		
8	CHA	0.075C	8:00H		2:00H
9	CHA	0.05C	7:00H		1:00H
10	DCH	0.05C	72V		2:00H
11	CHA	0.20C	3:30H		2:00H
12	CHA	0.10C	2:00H		2:00H
13	CHA	0.05C	11:00H		2:00H
14	STO				

The nominal values for current are again noted in fractions of the minimal capacity. Provided the paste is prepared with 10 to 15% red lead the formation will lead to an acceptable capacity. Without red lead a second discharge/charge cycle will give an improved performance.

Limited experience is available for transformation of the above program into voltage/amphour control. The following scheme according to table 16 should therefore be seen as a suggestion which requires experimental verification.

It would be very interesting to see whether savings in time result from this program and also, whether additional savings in total charge could be made due to the voltage control. To introduce a temperature control provides at least the advantage of making the alpha/beta PbO₂ relation more independent from the ambient conditions.

Table 16. Formation Proposal for Stationary Flat Plates

AM 15 g/Ah, Ch 360 Ah/kg = (5.4 C₁₀)

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<35C		
2	CHA	0.5I ₁₀	0.05C ₁₀	<2.8V/C	1:00 H
3	CHA	2.0I ₁₀ 2.6V/C 40°C	3.1C ₁₀		
4	CHA	1.2I ₁₀ 2.6V/C 40°C	1.9C ₁₀		2:00H
5	CHA	0.5I ₁₀	0.35C ₁₀		1:00H
6	DCH	0.5I ₁₀	1.8V/C		2:00H
7	CHA	2.0I ₁₀ 2.5/C	0.9C ₁₀		2:00H
8	CHA	0.5I ₁₀	1.0C ₁₀		2:00H
9	STO				

In order to become independent from the actual configuration and plate size the notations are given in multiples of the 10 h rate for the current and the nominal capacity for the charge amount respectively. V/C indicates Volts per cell.

5.3 Container Formation

Industrial batteries have much thicker container walls than automotive types. This makes the temperature problem in container formation even worse and artificial cooling is required to achieve reasonable charging times. For this the cells are assembled in containers for water cooling or are placed under water spray.

Most manufacturers allow for a discharge, mainly to make sure that all the cells meet the internal quality standards. Some improvement in the performance results, and this is important for stationary cells.

The most popular application is with traction batteries. The container formation of tubular plate cells is therefore shown as an example.

The plates are assumed to be made in the same way as in the example of tables 13 and 14. Using the same notation as in table 16 a typical program is given in table 17.

Table 17. Container Formation Tubular Traction Cells

Design Features as in Table 13

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<45C		
2	CHA	0.5I ₅	0.05C ₅	>2.8V/C	1:00 H
3	CHA	1.0I ₅ 2.6V/C 50°C	2.8C ₅		2:00 H
4	CHA	0.5I ₅ 2.7V/C 40°C	1.2C ₅		2:00H
5	DCH	0.5I ₁₀	1.80V/C		2:00H
6	CHA	1.0I ₅ 2.5V/C	0.9C ₅		2:00H
7	CHA	0.3I ₅	1.0C ₅		2:00H
8	STO				

The filling electrolyte should not be more concentrated than 1.23 g/ml otherwise the charge efficiency near the end of formation would be too low. The resulting specific gravity after step four is approximately 1.25 g/ml and so requires some addition of more concentrated acid, like 1.40 g/ml. This will not affect the plates as they include sufficient diluted acid.

The charge efficiency and performance can be improved significantly if a low concentration (1.10 g/ml) filling acid is used. Adjustment of the specific gravity then is more complicated. It can be made in multiple steps by addition of 1.400 and soaking off the excess fluid above the plates. Alternatively, the cells may be drained and refilled. The electrolyte which can be drained is some 50% of the total and the refilling specific gravity can be calculated accordingly.

It should be noted that the charge up to step 4 is in total with 4.05 C₅ only 135% of the theoretical value and so the capacity in the following discharge will be significantly lower than the nominal value. The discharge on the other hand helps to improve the state of performance more than simple overcharge.

The container formation of flat plate cells can be made in a very similar way. With the higher specific active material content the total charge must be increased to at least 4.5 C₅. While in general the current conversion efficiency in flat plate is lower, even this may not be sufficient, as much depends on the recipe and preparation as well as on the curing effectiveness. An example is given in table 18.

Table 18. Container Formation Flat Plate Traction Cells
Design Features as in Table 16

PS	Operator	Nominal	Switch	Break	Registration
1	PAU		<45C		
2	CHA	0.5I ₅	0.05C ₅	>2.8V/C	1:00 H
3	CHA	1.0I ₅ 2.6V/C 50°C	2.8C ₅		2:00 H
4	CHA	0.5I ₅ 2.7V/C 40°C	1.8C ₅		2:00H
5	DCH	0.5I ₁₀	1.8V/C		2:00H
6	CHA	1.0I ₅ 2.5V/C	0.9C ₅		2:00H
7	CHA	0.3I ₅	1.0C ₅		2:00H
8	STO				

The example is given with the provision of red lead added to the paste. If only lead oxide is used the current in step 3 should be reduced to, say, 0.7 I₅ and step four extended to 2.0 or 2.2 C₅.

5.4 Sealed Battery Specifics

Batteries called Sealed Lead-Acid (SLA) are becoming more and more popular for stand-by applications. The name is actually incorrect as they are designed to include safety valves which open irregularly to release unrecombined gas. Therefore they should be called "Valve Regulated" (VRLA) batteries rather than sealed.

Most manufacturers perform plate formation for this product despite the higher cost. Little container formation for this battery type is done and there is good reason for it. Here only UPS batteries of the absorbent glass mat (AGM) type will be discussed, therefore, exclude round cells with spirally wound electrodes as well as gel type cells, for reasons which will become quite clear as we explain further.

Top quality is a must for long term success of Sealed Lead Acid batteries. They must,

1. Provide an initial capacity of 100%
2. Be easy to interconnect safely

3. Have a service life of 10 years at rated capacity A good maintenance-free automotive battery, properly sized, could also be used. An application that requires daily charging for 20 minutes at 2.3 V/cell and recharging after infrequent power failure is well within the capability of a less expensive maintenance-free automotive battery.

5.4.1 Typical Design

In typical design the plates are much thicker than in automotive batteries (>4 mm) and the electrodes and separators are pressed together. The pores in plates and separators are only 90% filled with electrolyte in order to allow for the oxygen evolved on the positive plate to flow to the negative plate for recombination by diffusion in the g; phase. This means in practice that,

- the mass utilization is low
- the electrolyte exchange between plate and separate pores is negligible
- the gas release from the element is restrained

For complete understanding of the consequences and problems resulting from this for container formation one must refer to the basics, as described in 1.1.

Prior to formation there is an unavoidable soaking period where the electrolyte penetrates into the pores and the active material PbO (plus tri-basic and tetra-basic sulfate reacts to lead sulfate. The resulting decrease in pore volume is almost compensated for by the decrease in electrolyte volume and so only a small fraction of the mass can react, as the inter-plate electrolyte remains unchanged

The electrochemical reaction to PbO₂ and Pb in the positive and negative plates follows a solution-precipitation mechanism. With this the maximum reaction speed or maximum effective current depends on the amount of available lead sulfate. Using the automotive battery as a standard, the lack of lead sulfate is the first handicap for container formation of an AGM battery.

Provided we can achieve a reaction of the plates to the standard level of a tank formation, the pore volume in the positive plates remains practically unchanged, while it increases by a factor of some 1.3 in the negative plates, depending slightly on the actual recipe. This change is not compensated for by an equivalent increase of electrolyte volume. Note this is valid for formation PbO → Pb only, not for normal charge PbSO₄ → Pb. With the sensitivity of AGM batteries to the electrolyte volume this is the second handicap.

As there is no chance for recombination of hydrogen, its evolution must be suppressed, otherwise the equivalent capacity loss of the negative plates must be compensated by oxygen release from the cell resulting in water loss. So container formation must be voltage limited. Usually the mass ratio positive:negative exceeds 1.2 in AGM cells. With an amp-hour efficiency 100% for the negative plates (necessary) and 85% for the positive plates this gives a formation ratio of 0.85/1.2 = 0.71 at best, while a 90% Pt content is required. This is handicap number three.

There are ways and means such as starting with more diluted acid and adding more during formation, etc. to overcome or at least reduce the problems significantly. In any event container formation of sealed batteries is not state of the art and it is doubtful whether it ever will be feasible with respect to formation time and cost.

APPENDIX PLATE TESTS

1. GENERAL

Plate testing is performed by many battery companies to determine the quality of process methods as well as a specialized evaluation of actual plate performance.

While the tests which follow are considered traditional methods, variations of these methods may exist from manufacturer to manufacturer.

1.1 Principle

The maximum capacity of either a positive or a negative plate is determined with excess electrolyte and excess capacity of the opposite plate (counterplates). Standard batteries are almost always limited in capacity by electrolyte. Therefore, in these tests capacities are higher than realized for actual cells. Consequently, service life of the plates as tested is much shorter. The results are evaluated according to the method of a particular application. The methods include processing tests for R&D and quality control to evaluate production samples and production methods of industrial and automotive batteries.

1.2 Test Cells

Each test batch should include at least three units for industrial and six units for automotive batteries, where one unit consists of six cells. Therefore, for industrial plates, three units of six test cells for positive plate examination and three units of six test cells for negative plates are prepared. For the container, the smallest series which will hold the largest plate is selected.

Following the sketch given in figure 1, all connections and burned plate connections are made with wire of approximately 5 mm diameter before mounting plates into the container. At the top edges of the narrow container walls holes are made at each corner and one in the center opposite to the lugs of the counterplates. The diameter of these holes should be 0.5 mm less than that of the wire. The holes are cut open to the top of the container walls.

The plate supports are cut from 5 mm PVC sheet. The supports should be slightly higher than the bottom ridges in the container. Both supports are fixed by an ordinary PVC welding or glued in position. To avoid acid fumes the lid(s) belonging to the container(s) can be laid in place. Then the charge/discharge current supply to the test plates is fed through the vent plug openings.

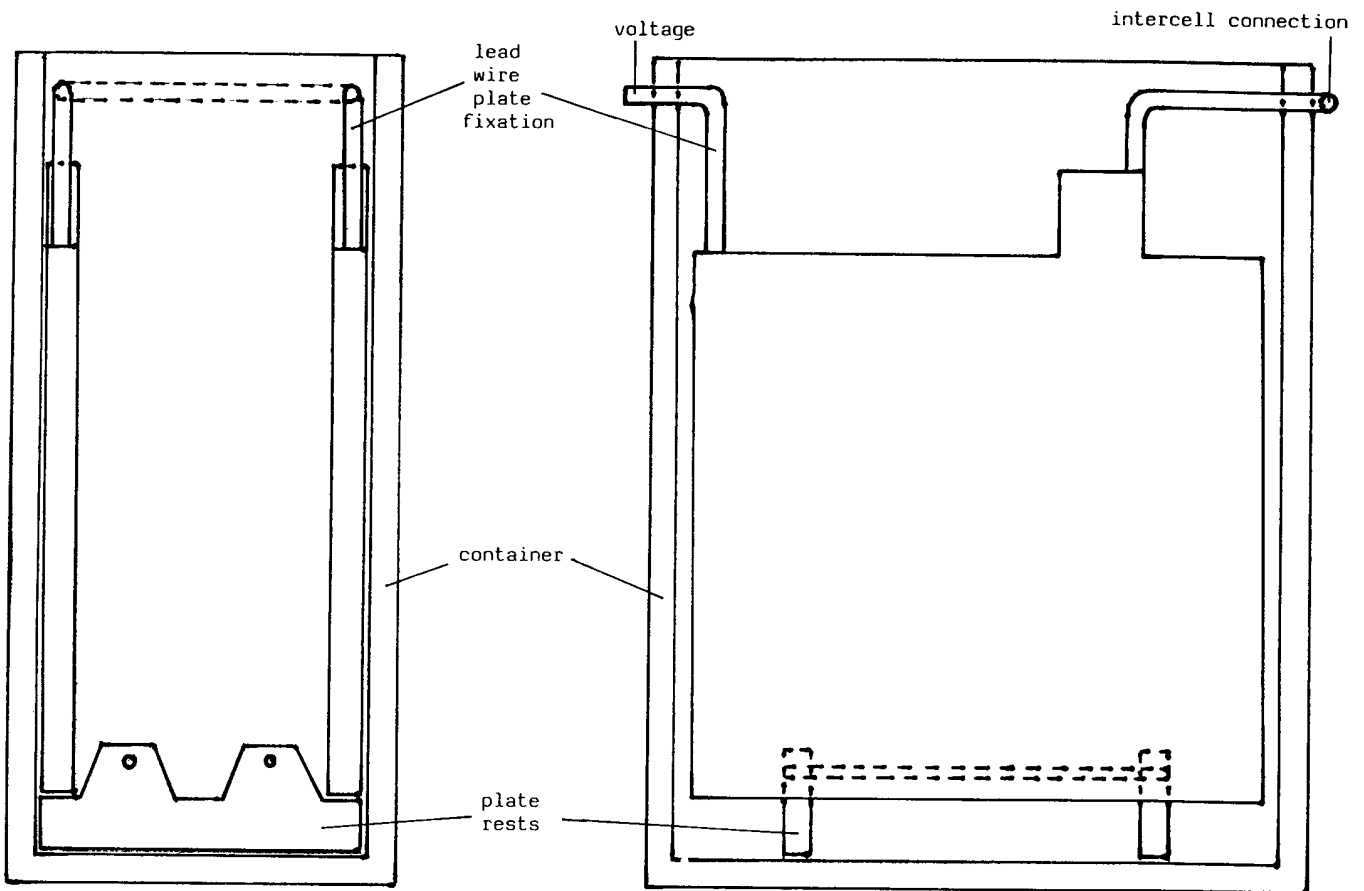


Figure 1. Plate Test Cell (with counterplates)

1.3 Test Plates

According to the presumed tests (see chapter 2.0), the plates are taken in the unformed, formed and wet, or formed and dried state. Two lead wires are burned onto the top edge of the lugs, one for the charge/discharge current the other for voltage reading (figure 2). This eliminates reading errors due to ohmic losses. Note that the results might differ from those observed with actual batteries.

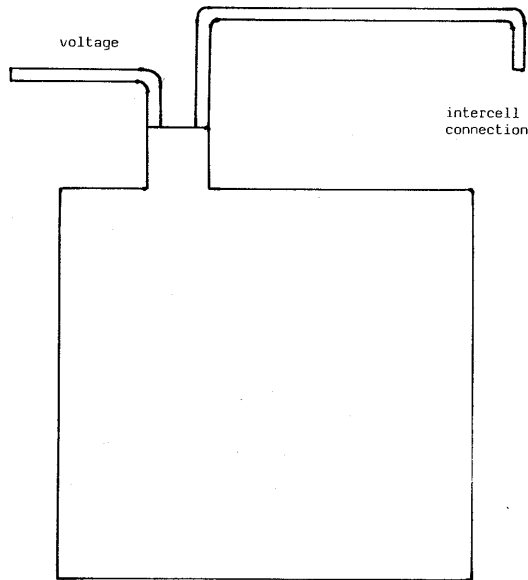


Figure 2. Welded Plate Connections

1.4 Initial Operation and Maintenance

The counterplates should be formed in the usual way before mounting in the cells according to figure 3. Auxiliary plates of the other polarity are prepared in the same way as the test plates and used for charging the counterplates to their full capacity.

If formed plates are used, the cells should be filled with nominal specific gravity electrolyte to the top ends of the lugs. The cells should get an overnight charge of at least the nominal capacity.

If unformed plates are used, the cells should be filled with electrolyte of the same concentration as used in the plate formation and the cells should undergo the same formation procedure. In this case the electrolyte will be replaced after formation by one of nominal specific gravity.

The auxiliary electrodes are stored carefully as they will be used again if,

- a) the test equipment has not been used for a week or more and the counterplates need an equalizing charge (0.1 x C per week)
- b) the test equipment is taken out of service for a longer period of time and therefore should be placed on float charge of 2.23 - 2.25 V/C.

c) the test plates are taken out after a discharge for analytical investigation in order to recharge the counterplates.

Note that the counterplates will not have an infinite life. Negative plates will show swelling and in most cases poisoning by antimony. They should be replaced when their actual thickness is twice the original value.

Positive pasted plates (flat plates) will lose active material due to shedding. Automotive plates should be replaced after a maximum of 40 tests, industrial plates after 100 tests. The service life of positive tubular plates might be several years.

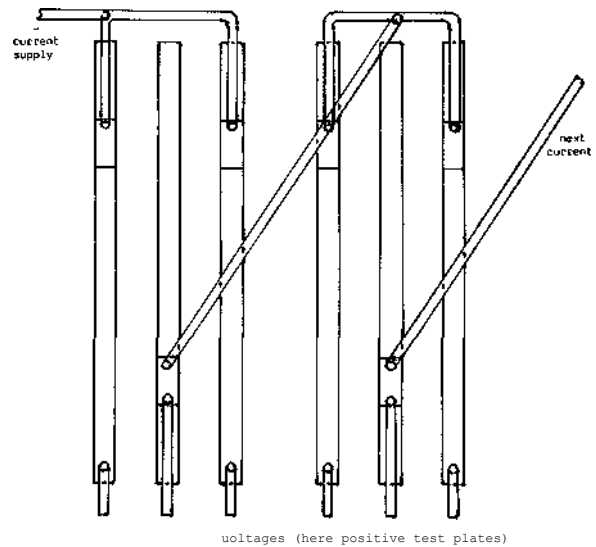


Figure 3. Intercell Connections

1.5 Electric Equipment

Digatron/FCI laboratory test equipment is recommended for these capacity tests because of its ability to totally satisfy Q.C. data requirements.

For R&D purposes where time-current profiles are required for both charge and discharge, the BTS-500 life cycle system should be considered. This system provides the optimum in automatic data collection with absolute accuracy.

For all tests it is necessary to monitor individual cell voltages. This is easily accomplished with the Digatron/F cell scanning feature added to the charge/discharge test unit.

2. CAPACITY TESTS

2.1 Quality of Formation

The test plates are taken from the formation tanks and immediately stored in plastic bags or with acid in suitable containers. Special care must be taken for negative plates so that no oxidation occurs while burning lead wires to each plate.

Discharge is made with the nominal currents, 20 hour rate for automotive, 5 hour rate for traction, and 10 (8) hour rate for stationary. The final voltage normally is set to 1.60 V other values may also be used.

In most cases it is an advantage to set internal standards for this kind of test. A two hour rate will provide both quick results and significant utilization of the mass.

The results are used for reference data of:

- quality of formation procedure (program, total ampere hours)
- active mass recipe
- curing procedure and parameters
- active mass utilization and minimum amount (preliminary values)

The results are also necessary to provide comparative data for the evaluation of the quality of the drying process.

With respect to the nominal capacity the results will be significantly different. In case of a lack of comparable data from previous plate tests, the following rates might be used for first assumptions for positive plates (negative plates in brackets):

20 h	discharge	130 (130) %	of nominal	automotive
10 h	"	140 (160) %	"	stationary
5 h	"	140 (150) %	"	traction
2 h	"	100 (110) %	"	automotive
2 h	"	105 (120) %	"	traction
2 h	"	95 (110) %	"	stationary

2.2 Quality of Drying

Plates dried after formation will lose part of their activity and/or Pb(neg.) and PbO₂(pos.) content. Analysis gives information about composition. Plate capacity shows the activity.

The test procedure is the same as described above. The results are compared with parallel data of the plate capacity after formation. Also the plates should be taken from the same batch for both tests.

A quality index for the drying is defined by Q_D
 $= \text{Capacity(dried)} / \text{Capacity(formed)}$

2.3 Development

The plates are inserted into the cells after curing and drying. The test is to be carried out according to the demands and goals of the R&D program. After formation, the result is checked by a discharge and in most cases one plate of the test set is removed for analysis.

Program parameters frequently investigated are:

- charge profile (timing)
- total current amount (Ah)
- acid concentration
- soaking time

The results of this test will be ideal, while the quality under factory conditions may be significantly different. But on the other hand, this is also a chance to see the difference with respect to the influence of temperature, increase of acid concentration and handling methods.

2.4 Barrier Layer Effects

Barrier layers result from an overdischarge of batteries with Sb-free or very low antimony grids in the positive plates. They will be recognized by the difficulties in recharging such batteries with limited voltage.

Investigation of single plate discharge and recharge with or without a rest in between is assumed to help provide a solution of actual problems. The test procedure has to be carried out according to preliminary assumptions and proposals.

3. CYCLING TESTS

3.1 Introduction

Plate cycling in most cases is made for accelerated life test of positive plates. Full utilization of the active mass due to an excess of acid is an important point of view in this respect.

The test arrangement is essentially the same as for the plate capacity test, but additionally, a separation is necessary in order to avoid early swelling and deterioration of the negative counterplates. A microporous separator is placed on the negative plate as usual and clearance to the positive test plates is maintained with spacers cut from perforated, corrugated PVC sheet, which is commercially available for industrial batteries.

Before starting the cycling, the plates should be checked for their initial capacity C(i) according to section 2.1.

3.2 Cycling Procedures

Full utilization of the active mass is realized by discharging the test cells to their breakdown voltage. In fact it does not make a significant difference whether the final voltage is 1.2 or 0 V/C. Since only the battery voltage can be taken for change of test step condition, an average of 0.5 V/C is recommended. The number of cells arranged in one test battery set will, of course, depend on the test program. Generally, at least three sample plates of each modification (amount of mass, recipe etc.) should be taken to make sure that the results are significant.

Discharge is made with the five hour rate approximately, but using the battery voltage (0.5 V/C) as the condition to switch to charging. The discharge current should be adjusted from time to time to the actual capacity rather than accepting continuously decreasing time periods.

Charge is made in two steps with constant currents. In the first step the battery is charged with the same current as used in discharge up to 2.4 V/cell. Then full charge is completed with 60% of the first current for 2.5 hours. The charging factor is 120%.

Each cell voltage should at least be recorded during discharge but preferably for a full cycle according to the expected lifetime. The following recommendations are given in case no better data is available:

Life-time is defined by deterioration of the capacity down to e.g., 50% of the initial value C(i). The expected life is
 20 to 50 cycles for automotive plates
 100 to 300 cycles for pasted (flat) industrial plates
 300 to 800 cycles for tubular plates

Note that the actual cycle life is also dependent on the quality of the grid casting!

Whenever single plates reach the end of life, they should be removed and the test continued with a reduced number of cells as long as further valuable information can be obtained.

3.3 Evaluation

As plate cycling is a comparative test no information should be expected with respect to actual service life of fully sized batteries. Plate cycling is a screening test only, so the relative advantage or disadvantage can be seen of different production methods, materials or recipes.

3.3.1 Electric Properties

For proper evaluation of the test (graph of actual capacity versus cycle number) one should have a minimum of 10 points. With BTS-500 life cycle test systems, all cycle performance information is recorded.

The graphs will show the relative behavior of cells or batteries having the same product parameters under severe cycling conditions as long as the plates tested (either positive or negative) are truly the ones limiting service life. The graphs will also give reasonable information for moderate cycling but nothing concerning standby application.

For final evaluation the information from visual inspection and if possible, from chemical analysis should be taken into account.

3.3.2 Visual Examination

Pasted positive plates should first be examined for loss of active material due to shedding. Presumably, the initial weight $AM(i)$ after formation is known directly or via calculation from the pasting data. The first information is given by the active mass weight $AM(t)$ after test. The ratio,

$$Q(1) = AM(t) / AM(i)$$

is another indicator together with the capacity for the active mass quality if compared with other plates of the same or similar tests with the same amount of cycles. This is true as long as the latest data for the actual capacity $C(t)$ does not

show a large discrepancy in relation to the initial one $C(i)$ given by

$$Q(2) = C(a) / C(i)$$

In case the ratio of $Q(2)/Q(1)$ is higher than 1.1, it is assumed that the processing (paste recipe, curing, formation) should be modified such that low initial performance not accepted due to other reasons.

If $Q(2)/Q(1)$ is lower than 0.8 either barrier layer effect deterioration of active mass composition (chemically or physically) should be taken into account particularly when the maximum capacity exceeds the initial capacity by more than 10%. Another reason might be lack of good electrical contact. This is not only found when the positive plates enveloped in pocket separator, but also in standard design. Washing off the mass with poor adherence by using jet flowing water will show the really active part that is still adhering to the grid.

Inspection should always also be made for grid corrosion. A check of the dimensions will show the amount of elongation which indicates intergranular corrosion. Fractures in most cases are due to casting faults especially when found in the grid frames. The absolute corrosion rate is determined by the weight difference between a new grid and one after test and etching off of the corrosion layer.

Negative plates will show extreme swelling in this type test. Additionally, voltage reversal may occur frequently causing brown spots of PbO_2 to be found on the surface of the plates. These effects make visual examination very difficult and will not give clear results in many cases. Side plate cycling is made for negative plates, in most cases done for expander testing with electrical data the most valuable parameter for evaluation.

Table I. Sulfuric Acid
1. Properties

Content %wt	Specific Gravity g/ml (20°C)	Electrochemical Equivalent Ah/liter
6	1.037	17.0
8	1.050	22.9
10	1.064	29.1
12	1.089	35.4
14	1.092	41.9
16	1.107	48.4
18	1.122	55.1
20	1.137	62.0
22	1.152	69.3
24	1.167	76.5
26	1.183	84.0
28	1.199	91.5
30	1.215	99.5
32	1.231	107.2
34	1.248	116.8
36	1.264	124.0
38	1.281	133.0
40	1.299	141.9

2. Purity Requirements For Battery Acid
(DIN 53510) (SP.GR. 1.20... 1.30 G/ML)

Impurity	Max. mg./l
Platinum	0.05
Copper	0.5
Other metals of H ₂ S group single	1.0
total	2.0
Cr, Mn, Ti each	0.2
Iron	30.0
Other metals of Amm.sulfide single	1.0
total	2.0
Halogen, total	5.0
Nitrogen (NH ₃)	50.0
Nitrogen (NO ₃)	10.0
SO ₂ or H ₂ S	20.0
Volatile organic acids	20.0
Permanganate number	30.0
Residue o. ignition 700/800°C	250.0

Table II. Lead and Lead Compounds

1. Lead	Max. mg./l
Density 25° C	11.34 g/ml
327° C (solid)	11.06 g/ml
327° C (liquid)	10.69 g/ml
Heat Capacity 25° C	128 J/Mole * kg
Specif. Resistance	2.07x10 ⁻⁵ Ohm*cm
Atomic weight	207.2
Iron	30.0

2. Lead Compounds

Compound	Density 25° C g/ml	Heat Capacity J/kg Mole	Mol. Weight
PbO	9.35	205	223.2
Pb ₃ O ₄	9.1	214	685.6
Beta PbO ₂	9.5	270	239.2
3PbO*PbSO ₄	7.0		990.8
4PbO*PbSO ₄	8.1		1196.0
PbSO ₄	6.3	342	303.3
H ₂ O	1.0	4181	18.0